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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for U. S. ATOMIC ENERGY COMMISSION by ARGONNE NATIONAL LABORATORY

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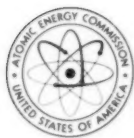
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REACTOR FUEL PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

Prepared for U. S. ATOMIC ENERGY COMMISSION
by ARGONNE NATIONAL LABORATORY



- APRIL 1961
- VOLUME 4
- NUMBER 2

foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Office of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering Division. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., A. A. Chilenskas, I. G. Dillon, P. Fineman, J. Fischer, A. A. Jonke, S. Lawroski, W. J. Mecham, J. Royal, J. H. Schraidt, W. B. Seefeldt, V. G. Trice, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

S. LAWROSKI

*Director, Chemical Engineering Division
Argonne National Laboratory*

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Section

I

COMMERCIAL ASPECTS OF FUEL PROCESSING

Industrial Participation in Fuel Processing

Some results have recently become available on the study of the feasibility of a privately owned plant to process spent power-reactor fuels.^{1,2} The study was made by Davison Chemical Division of W. R. Grace and Company for the Industrial Reprocessing Group (IRG), made up of five utility companies along with Davison. The IRG study recommended a plant with a capacity of 1 ton per day, operating 300 days per year. The small, compact plant would occupy about 15,000 sq ft and would be capable of processing all the power-reactor fuels of current interest. It was said that an annual work load of only 200 tons would sustain the plant's operation, at prices warranting operation of the plant. Since only 150 processing tons were to come from the participating utilities that would be committed to pay for a certain load whether used or not, an additional 50 to 75 tons would have to come from other sources.

After discussing participation with other companies, Davison informally advised the U. S. Atomic Energy Commission (AEC) in October of the probable need for 50 to 75 tons of spent fuel per year from government reactors to meet the 200-ton-per-year schedule. The AEC pointed out that it would be necessary to solicit proposals on an industry-wide basis whenever the AEC determined that a specific base load was to be made available.

The next step in the IRG plan would be the preparation of a detailed engineering design study by Bechtel Corp. (to which each of the five industry sponsors would contribute \$100,000) to arrive at guaranteed capital costs of the plant. Of the five utility members of the IRG, three

have indicated a willingness to proceed. The remaining two members would delay participation in the project for at least two years, thus, in effect, withdrawing from it, at least for the time being. The two withdrawing members, Commonwealth Edison Company and Yankee Atomic Electric Company, based their decision on dissatisfaction with the economics of the proposed plant. The proposed IRG prices were said to be 20 per cent higher than the processing cost schedule established by the AEC. The two utilities recommended a two-year delay to accumulate a stockpile of spent fuel in order to assure a load factor that would keep unit costs low. This would apparently require that the AEC's 4 per cent use charge on the fuel be waived during the storage period. The capital cost of the plant is reported to be estimated at \$20 million to \$23 million, instead of the \$12 million to \$15 million originally estimated. In order to provide the minimum load commitment of 200 tons per year, Davison has invited other utilities, as well as Westinghouse Electric and General Electric, to join the processing group.

Although a determination by IRG of its intent to proceed with such an enterprise was originally expected to be reached by July 1960, it now appears that such a decision is sometime in the future.

In the interim (since the first IRG announcement in November 1959), the AEC has continued to study alternate ways in which these power fuels could be processed at AEC facilities. It has been determined that, in the over-all interest of economy, the processing should be consolidated at fewer sites than was previously planned. Generally, it has been decided that the low- and intermediate-enrichment fuels would be assigned to Savannah River and high-enrichment fuels to the Idaho Chemical Proc-

essing Plant (ICPP). These reassignments result in reduced over-all costs and still retain in the AEC processing plants adequate separation capacity to meet program needs.

The AEC is hopeful that processing services will become available from private companies in facilities financed by private capital. Pending further information on the conclusions of the IRG regarding a possible private plant, the AEC has continued to hold in abeyance the modification of existing processing plants to process the power fuels as outlined above. It will, however, install facilities at Savannah River which will permit the receipt and handling of the off-site fuels. Adequate receiving and handling facilities are available at ICPP.

Certain of the reactor operators whose fuels had previously been assigned to Hanford Atomic Products Operation (HAPO) have been advised that responsibility for the acceptance of their fuels by AEC has been reassigned to Savannah River.

John A. McCone, in a statement while he was still chairman of the AEC, said: "We dislike going into the reprocessing of industrial fuels because it puts us into this business. Once you're in the business, it's hard to get out. However, we made a commitment to the industry and have a moral obligation to arrange to reprocess their fuels. We intend to do this, but we want to give the industry every encouragement. We are perfectly willing to consider having the industry process our unclassified cores." He pointed out that there are several private organizations interested in getting into the processing business, and, he said, "I am very, very hopeful that someone will come forth with an acceptable plan We can wait a few months . . . [before we have to move ahead with our own plans to handle industrial fuels]."³

Unrelated to the above plans for spent reactor fuels is a recent announcement that the commercial-scale purification and fabrication of U^{233} will be undertaken by Davison at its Erwin, Tenn., plant under a contract with Atomics International (AI) to produce fuel for AI's Advanced Epithermal Critical Assembly. The contract calls for purification, conversion to oxide, and fabrication into aluminum-clad platelets. Purification will be by dissolution in acid and solvent extraction behind concrete. Remote handling³ is required because of the radioactive daughter products built up in U^{233} .

Foreign Government Processing Programs

Construction of a second chemical processing plant in France has been scheduled to start next year. The new plant will be located at Cap de la Hague on the tip of the Normandy peninsula near Cherbourg. France's first processing plant is located in southeast France at Marcoule. At the proposed plant, plutonium will be extracted from fuel elements irradiated in three gas-cooled graphite-moderated natural-uranium power reactors of the French national electric utility, and the 100-Mw(e) natural-uranium heavy-water reactor on which the French AEC expects to start construction late this year or early next year. All four of the above reactors are in northwestern France.⁴

Eurochemic (European Company for the Chemical Processing of Irradiated Fuels) is planning a two-stage approach in designing the irradiated fuel-processing plant to handle spent fuel elements from the 13 European nations participating in the project at Mol, Belgium. The first stage calls for a multipurpose dissolver for batch or semicontinuous operation with fuels enriched up to 1.6 per cent. Later a semicontinuous unit geometrically safe for enrichments up to 5 per cent will supplement the first dissolver. The flow sheet for the plant calls for a two-cycle Purex process using a 30 per cent solution of tributyl phosphate in hydrocarbon diluent. Construction³ is scheduled to start in the summer of 1961 for operation in 1964.

Gas Centrifuge Separation of Uranium Isotopes

Because of the current interest in the gas centrifuge method for separation of uranium isotopes, the AEC recently issued two press releases on this subject, one of which includes a report on the status of gas centrifuge technology in the United States and abroad.⁵ The principle of the gas centrifuge is to pass uranium in gaseous form (uranium hexafluoride) through a centrifuge that spins at very high speed, allowing separation of the isotopes because of their slight difference in weight. Two possible advantages of the centrifuge method over the gaseous diffusion process are its po-

tential lower electric power requirement and its potential requirement for fewer units in series to produce the desired enrichment of U^{235} . Further, it appears to be particularly well suited for low-capacity installations.

Theoretically, the separative work performed varies with the fourth power of the centrifuge speed. Thus doubling the speed would, in theory, increase the separative work performed by a factor of 16. As progress is made in construction materials and designs which permit higher speeds, enthusiasm rises for the application of this process in separating uranium isotopes.

General areas in which problems still must be solved include the following:

1. Demonstration of the reliability of present experimental machines for continuous long-term service with UF_6
2. Development of a machine satisfactory for mass production of identical units
3. Development of a method for the introduction and removal of gas when machines are connected in series
4. Determination of auxiliary processes, services, and instrumentation necessary for plant operations

The AEC's planned program in gas centrifuge technology includes three major areas: (1) continuation of basic research at the University of Virginia, (2) experimental operation of small groups of machines at the Oak Ridge Gaseous Diffusion Plant, and (3) proposed development work by private companies to develop advanced models of gas centrifuges. The total AEC effort is expected to be at a level of \$2 million to \$3 million per year.

Since a number of private companies have indicated a belief that there is substantial commercial potential in the centrifuge process to provide fuels for nuclear reactors, the AEC has proposed an amendment to AEC regulations to extend the access permit program to allow private industry to work in classified areas of the gas centrifuge field. This action would permit industry to employ private funds and to retain the benefits of its work in this area.⁶

The technology of gas centrifuge separation is not now developed to a point where this process is competitive with the current gaseous diffusion process. On the other hand, projections of possible gains in the centrifuge process indicate that the process may become economically attractive in the future.

Uranium Concentrate Prices

The AEC has published detailed information on both prices and commitments for all 27 of its domestic uranium suppliers. The prices for deliveries to be made before Mar. 31, 1962, range from a low of \$7.46 to a high of \$10.70 per pound of contained U_3O_8 . The price variations are due to such factors as type of treatment process, quality of ore processed, and size and location of mill. For domestic uranium concentrates⁷ contracted for delivery in the period beginning Apr. 1, 1962, and ending Dec. 31, 1966, the AEC has established a flat price of \$8 per pound of contained U_3O_8 .

The above prices may be compared with the competitive bids made by some 16 foreign and domestic uranium producers for an order of 13 metric tons of concentrates for the Japan Atomic Fuel Corp. An order for 6.5 tons was placed in May 1960, and a second order for an equal amount was placed in October 1960. For the May order the bids⁷ ranged from \$4.90 to \$5.82 per pound of contained U_3O_8 , and for the October order, from \$4.37 to \$6.65.

AEC Commissioner Loren K. Olson recently stated that, for both strategic and economic reasons, the maximum utilization of domestic uranium resources has been a continuing AEC objective. Domestic production in the current fiscal year will be at an all-time high of about 18,000 tons of U_3O_8 . Fiscal year 1962 receipts are estimated to be at about the same level.²

Charges for Commercial

Use of Plutonium

The AEC has recently increased the charges for commercial-industrial use of plutonium in instrument components such as plutonium-beryllium neutron sources.⁸ The base charges are now equal to the prices that the AEC will pay for this material purchased from reactor owners, namely, \$30 to \$45 per gram (depending on Pu^{240} content) until June 30, 1962, and \$30 per gram from July 1, 1962, to June 30, 1963. No charge has been established beyond that period.

Plutonium-beryllium sources serve as a spontaneous source of neutrons and are used in oil-well exploration, calibration of nuclear instruments, and to initiate the chain reaction in

nuclear reactors. Since plutonium may be distributed domestically only under lease from the AEC, the effect of the new change will be to increase the use charge paid to the AEC, currently 4 per cent of the plutonium value per year. No base charge has yet been established by the AEC for the use of plutonium as fuel for nuclear reactors.

Waste-Disposal Licensing

Representatives of the city of Antioch, Calif., recently objected to the AEC about the waste-disposal activities of the Nuclear Engineering Company, which uses a site near the city's part-time source of water in the San Joaquin River. To preclude possible contamination of the city's water supply through accidental leakage from waste-disposal drums, the AEC requested the Company to agree to a license change prohibiting use of the site. Nuclear Engineering requested a hearing and later met with representatives of the city, the state, and the AEC. A tentative agreement was reached whereby Nuclear Engineering would not load its waste-disposal barge while the city was using the river as a source of water supply (a situation that occurs irregularly because of salt-water contamination of the stream). An amended license is being prepared for consideration.^{2,4}

The French government recently encountered the first widespread public opposition to its nuclear waste-disposal program when the French AEC announced its intention of disposing of 6500 barrels of low-level radioactive wastes in the Mediterranean. The proposal met with opposition from officials of the French resort area. The government agreed to postpone the disposal activities, although it said that the disposal involved no danger and that, even if the barrels were breached, the resultant escape of radioactivity would be far below permissible levels.²

Land Burial

The AEC is amending its regulation on Standards for Protection Against Radiation to reflect

its policy on land disposal of low-level packaged radioactive waste materials.⁸

Under the existing *Code of Federal Regulations*, Title 10, Part 20, licensees are permitted to dispose of very low concentrations of radioactive waste by burial in the soil. The amendment to this Section 20.302, which became effective Feb. 17, 1961, permits licensees to continue this practice, but it states that the AEC will not approve an application for a license to receive radioactive waste material from other persons for disposal on land not owned by the state or federal governments. To date, the AEC has not issued any licenses to receive waste materials from other persons for burial on nongovernment-owned land.

In January 1960 the AEC announced that it had determined that regional sites for the permanent disposal of low-level radioactive waste would be established, as needed, on state or federal government-owned land.¹⁰ The AEC has made available its land burial sites at the Oak Ridge National Laboratory (ORNL), Oak Ridge, Tenn., and at the National Reactor Testing Station (NRTS) near Idaho Falls, Idaho, for the disposal of low-level wastes by AEC licensees.

References

1. *Nucleonics*, 18(12): (December 1960).
2. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., 7(11): (November 1960).
3. *Nucleonics*, 18(11): (November 1960).
4. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., 7(10): (October 1960).
5. Statement by John A. McCone, Chairman USAEC, on Status and Prospects of Gas Centrifuge Technology, AEC Press Release C-253, Dec. 13, 1960.
6. AEC Proposes To Extend Access Permit Program To Permit Development by Private Industry of Gas Centrifuge, AEC Press Release C-252, Dec. 13, 1960.
7. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., 7(12): (December 1960).
8. AEC Announces Base Charges for Commercial Uses of Plutonium, AEC Press Release C-239, Nov. 29, 1960.
9. AEC Amends Regulation on Land Burial of Low-Level Radioactive Waste, AEC Press Release D-4, Jan. 5, 1961.
10. *Reactor Fuel Processing*, 3(4): (October 1960).

Section

II

SAFETY IN CHEMICAL PROCESSING

Redox Multipurpose

Dissolver Incident

A final report has been issued¹ on the Redox multipurpose dissolver incident, described in an earlier Review,² in which a combination of fires and pressurizations took place in a uranium metal dissolver in the Redox plant at Hanford on Apr. 17 and 18, 1960. It was conclusively established that the incident was not a criticality accident. No exposure of personnel and no release of activity to the building or the environs occurred. However, contamination of the dissolver cell and the loss of the dissolver resulted from the incident. Reference 3 describes the multipurpose dissolver, and a cutaway of the dissolver is shown in Fig. II-1.

The dissolver was designed to provide (1) a critically safe vessel for dissolving uranium metal containing up to 1 per cent U^{235} , (2) a vessel that could be charged with fuel elements up to 10 ft long, (3) an off-gas arrangement that would eliminate the return of ammonia to the dissolver during the Zirflex decladding process, (4) a means of dissolving small charges without using extra chemicals, and (5) a bypass routing around the silver reactor (used for trapping volatile radioactive iodine) during cladding removal. These requirements were met by a dissolver having a fuel annulus with an inside diameter of 4 ft 1 in., an outside diameter of 5 ft 10 in., and a height of 9 ft 6 in. (to the bottom of the slug charging cone). Other details of the dissolver and off-gas system are given in reference 3. In actual performance the dissolver exceeded design capacity, both in instantaneous dissolution rate and in sustained capacity.

At the time of the incident, the dissolver contained bare, irradiated uranium metal. One-half of the metal was covered with water, whereas

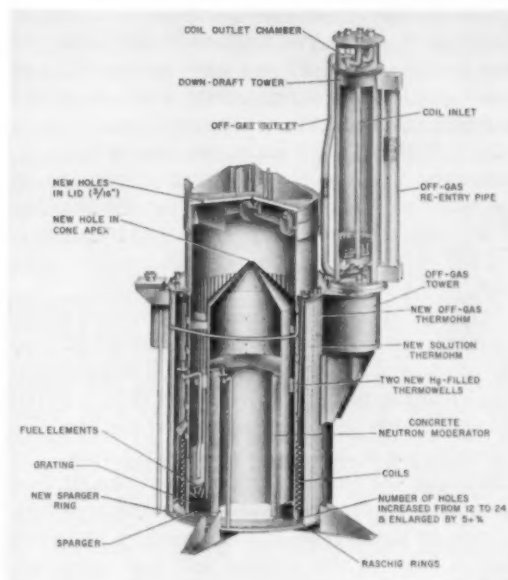


Fig. II-1 Sketch of Redox multipurpose dissolver.

the other half was exposed to the moist air above the water surface in the dissolver for a 30- to 36-hr period preceding the incident.

The first indication of trouble was observed on April 17, when the off-gas temperature began a gradual increase from 25°C at 10:00 a.m. to 52°C at 2:30 p.m. At noon the temperature of the water in the dissolver was 60°C. By 2:40 p.m. the temperature of the water had increased to 86°C. Moreover, the vacuum in the dissolver was lost through vaporization of the water from the water seal around the dissolver lid. The vacuum was regained when the water seal was refilled; however, a momentary pressurization occurred during this operation. The solution temperature was reduced to about 50°C, the

normal temperature, by passing water through the internal cooling coils of the dissolver. Another rise in the temperature of the solution occurred, and the solution was again cooled to the normal temperature by means of the cooling coils. Starting at 3:30 p.m., frequent pressurizations occurred, and a consistent vacuum was difficult to maintain. By 5:00 p.m., however, the vacuum was reestablished.

At 6:45 p.m., after the solution in the dissolver was heated to 75°C by mistake and again cooled to the normal temperature by means of the cooling coils, the solution in the dissolver was removed, and 47 per cent nitric acid was added until the uranium metal in the dissolver was half covered. Almost immediately the specific gravity of the solution increased to >1.85 , indicating that the concentration of uranium in the solution was $>2.5M$. Following the addition of the acid, the dissolver pressurized frequently, and the dissolver vacuum was not reestablished until 7:40 p.m.

With the vacuum regained, the contents of the dissolver were heated to boiling, and at 8:30 p.m. the addition of 60 per cent nitric acid was started. The reaction became so vigorous after a small amount of the acid had been added that the dissolver vacuum was nearly uncontrollable. The addition of the acid was stopped, and a small flow of cooling water was started to the dissolver coil. A rise in liquid level in the dissolver indicated that a leak in the cooling coil had occurred.

Dissolver operation became more erratic, and at 8:45 p.m. a rumbling was heard in the dissolver cell. At the same time, the dissolver vacuum was completely lost. A full flow of water to the cooling coil was started. The second and third rumbles were heard at about 15-min intervals. At this time, the liquid level in the dissolver was twice as high as it had been. The flow of the cooling water was stopped; whereupon the liquid level in the dissolver started to drop immediately, and the sump liquid level began to rise. The sump solution was found to be about $0.3M$ uranium. The gamma radioactivity of the cell exhaust increased 300-fold above normal between 6:30 and 8:30 p.m.

At 1:30 a.m. on April 18, the cell cover was removed, and a 10-min inspection of the cell interior was made. The inspection disclosed that, although the dissolver lid was still on top of the vessel, the lid was inverted and was 1 to 2 ft off center. The underside of the lid was discolored; the remainder of the cell, however, ap-

peared clean. No other visible damage was apparent.

At 4:00 a.m. the temperature of the dissolver off-gas began to rise and continued to increase until it reached a peak of 35°C by 4:00 p.m. During this period the gamma radioactivity of the cell off-gas began to increase. From these observations it became apparent that a resumption of the reaction in the dissolver was occurring. At 7:30 p.m. a large quantity of water was added to the dissolver as rapidly as possible. Despite the partial opening provided by the displacement of the dissolver lid, a pressurization of the dissolver was observed. The off-gas temperature rose sharply and then dropped steadily to a temperature of 23°C by 3:00 a.m. on April 19. The gamma radioactivity of the cell exhaust air rose to a maximum at 100 times normal between 4:00 and 8:00 p.m. on April 18 and then rapidly dropped back to normal.

At 10:00 a.m. on April 19, the cell cover was removed again for the purpose of replacing the dissolver cover in its proper position. The attempt to replace the cover was abandoned when the activity of the air in the canyon increased. While the cell cover was off, it was noted that the cell was covered with a fine dust. The cell cover was replaced, and the cell remained closed until the problems of contamination could be brought under adequate control.

Cleanup

The first step of the cleanup was to wash the canyon with water by means of canyon roof sprays. This was followed by flushing the canyon deck with water. The crane was decontaminated next by means of solvent sprays.

A backup filter was installed downstream from the dissolver off-gas filter to minimize the possibility of discharging the radioactivity to the atmosphere and environs. After the emergency backup filter had been installed, three spray nozzles were used to wash the dissolver cell. A water spray was installed around the top of the cell to provide an umbrella of water above the cell opening. The cell cover was then removed without any measurable recontamination of the canyon or the crane.

At this time the old dissolver lid was replaced by a new one through which passed a water addition line and two temperature-sensing elements, one for the vapor phase and the other for the metal-containing annulus. A sample was re-

moved for neutron-activation detection. A 20 per cent solution of nitric acid was then used to remove soluble sludge from the cell floor.

The dissolution of the uranium remaining in the dissolver was carried out in two steps. First, 20 wt.% nitric acid was added to the dissolver mixture. The dissolution rate was rapid, and stoichiometric calculations indicated that the material being dissolved was a mixture of UO_2 and U_3O_8 . In the second step, the concentration of the acid was cautiously and progressively increased. During this period, temperatures rose suddenly on two or three occasions, requiring the "drowning" of the reaction. These thermal excursions were accompanied by the formation of hydrogen, which suggested that small-scale fires might be involved. The dissolution of the uranium was continued until the dissolver was emptied.

A new lid with a circulator for decontamination chemicals was installed over the dissolver opening, and seven 5-hr recirculation flushes were applied to the interior of the dissolver. After the dissolver had been cleaned, a remote television camera was used to inspect the interior and exterior of the dissolver. At least two holes were seen in the wall of the inner cylinder below the base of the distributor cone. Near the bottom of the annulus, several irregularly shaped masses, resembling welding slag, were observed.

After the condition of the dissolver had been ascertained, the dissolver was removed from the Redox plant to a decontamination facility. Closer inspection confirmed the presence of two large oval-shaped holes (12 to 18 in. wide and 2 to 3 ft long). An inspection of the metal edges of these holes indicated that the damage probably resulted from high temperatures rather than from high pressures. A slit in the dissolver cooling coil was also seen.

One of the pieces of slag found in the dissolver was analyzed chemically. The results revealed that the composition of the sample was as follows: 72 per cent iron, 9 per cent chromium, 11 per cent nickel, and 8 per cent uranium. Phase diagrams indicate that temperatures $>1300^\circ\text{C}$ existed in regions of the dissolver during the incident.

Causes of the Incident

Analysis of all available information indicated that the incident was most probably caused by a

chemical reaction. Proof that the incident was nonnuclear in origin was derived from two sources of data. First, an estimate was made of the number of fissions which would be required to provide the energy necessary to bring the dissolver contents to the temperatures recorded during the incident. An estimate of the increase in gamma activity, which would accompany a nuclear reaction of the calculated magnitude, ruled out the possibility of a nuclear incident since the actual change in the gamma activity was very much smaller than the estimated value. Further proof that the incident was nonnuclear was provided by two samples of material removed from the cell. The samples were examined for neutron-induced activity, and the negative results that were obtained proved conclusively that the incident was not a criticality accident.

The following explanation of the incident has been proposed:¹ After partial dissolution of the uranium slugs, the remaining metal had an etched surface that provided a greater area-to-volume ratio than that of the original material. The metal was gradually heated by fission-product decay heat and was not adequately cooled because half the metal was exposed. The poorer heat dissipation due to annular geometry and slug packing, compared with a standard vessel, permitted the temperature of the exposed metal to increase to about 80 to 150°C . In this temperature range the reaction of uranium with oxygen and water vapor became significant. The heat of the reaction, combined with the fission-product decay heat, raised the temperature to about 300°C . At this temperature the oxidation reactions became rapid, and ignition of the metal occurred with temperature excursions as high as 1300°C .

The heat generated by the reaction was also transmitted to the metal below the liquid surface. This resulted in a rapid increase in the temperature of the solution. The temperature of the dissolver walls also increased, and this, in turn, accelerated the evaporation of water from the lid water seal. The loss of the dissolver vacuum followed. In the attempts to reestablish the lid water seal, water was poured on the hot exposed material in the dissolver, causing hydrogen evolution.

During the course of the reactions, considerable amounts of UO_2 and U_3O_8 were produced. On addition of 47 per cent nitric acid, the oxides dis-

solved rapidly. Frequent pressurizations occurred during this dissolution.

The dissolver cooling coil apparently failed at about 8:20 p.m., 10 min before the addition of the 60 per cent nitric acid was started. The coil failure resulted in a flooding of the dissolver. The pressurization and rumble that followed probably resulted from the sudden quenching of hot metal and the rapid reaction between the uranium and water. Ignition of hydrogen may also have been a contributing factor. The pressurization that occurred during the third rumble (9:05 p.m. on April 17) was of sufficient magnitude to invert the 6-ft-diameter dissolver lid.

The fire was quenched by the water leakage through the ruptured cooling coil. After the water was turned off, half the uranium was again exposed to the atmosphere as the solution drained off through the holes in the dissolver wall.

The uranium required only 8 hr to reignite (at about 5:00 a.m. on April 18). The metal was probably activated by the previous water quench because of hydride formation and the disruption of the oxide scale. The fire was quenched 15 hr later; the violence of the ensuing reaction pressurized the dissolver and carried fine oxide scale into the dissolver cell. The majority of the contamination problems were caused by this oxide scale.

Property damage to the dissolver was estimated to be \$103,000, and replacement costs were estimated to be \$118,000. Restoration and cleanup costs¹ as of Sept. 18, 1960, were \$124,000.

Recommendations

As a result of the incident, the following recommendations were made:¹

1. Resume Redox plant operation with conventional dissolvers, modifying procedures to conform to the recommendations that follow.
2. Liquid should completely cover the solid fuel (clad or dejacketed) in the dissolver as continuously as possible, and certainly when the holding period for a charge is to exceed 8 hr.
3. The dejacketed fuel elements should be submerged, in so far as physically possible, throughout the dissolution step.
4. New dissolvers should be provided with instrumentation to measure the temperature of the vapor leaving the dissolver vessel.
5. New dissolvers, in which relatively uniform orientation of fuel elements can be anticipated, should be provided with instrumentation to measure temperatures adjacent to the fuel crib.
6. Although the primary gas filter contained the radioactivity in this incident, the installation of a permanent backup filter was recommended for all dissolvers where there is any possibility that the primary filter might not retain all the radioactivity that might arise in any situation.

References

1. M. K. Harmon, Redox Dissolver Incident: A Comprehensive Report, USAEC Report HW-66850, Hanford Atomic Products Operation, Sept. 13, 1960. (Classified)
2. *Reactor Fuel Processing*, 3(4): 7 (October 1960).
3. H. P. Simonds, Multi-Purpose Dissolver Information Manual, USAEC Report HW-64172, Hanford Atomic Products Operation, Mar. 4, 1960.

Section III

PREPARATION FOR FUEL PROCESSING

The wide variety of nuclear reactor fuels requires development of numerous "head-end" processes to produce fuel solutions compatible with existing processing plants. Some head-end processes remove the cladding separately, and others put cladding and fuel into a single solution. Mechanical decladding, chemical dejacketing, dissolution, and precipitation are discussed in this section.

Mechanical Processing

Inasmuch as many of the claddings of nuclear fuels are chemically resistant, it is often desirable to remove the cladding material mechanically. The important advantages of mechanical processing include production of smaller aqueous waste volumes, use of less corrosive reagents for dissolving the fuel material after the cladding is removed, and increased plant capacity in the absence of dissolved cladding material in process streams.

Two Savannah River reports that describe shearing of irradiated uranium plates have been declassified.^{1,2} Three aluminum-clad plates of natural uranium which were irradiated to 600 and 1500 Mwd/ton were cut easily to short lengths with a guillotine type shear.¹ The maximum force required to cut an irradiated plate 0.180 in. thick by 3.1 in. wide was 18,000 lb, which is less than half of the 41,000 lb required for unirradiated material. Crumbling of the plate was reduced to an average of 1.4 g of fragments per cut by employing a near-vertical shearing action rather than the scissors type action of standard portable shears. Also cut were ten additional plates that had been irradiated to either 480 or 940 Mwd/ton average exposure and had cooled from 12 to 16 months.² Each plate was about 3 in. wide by 0.2 in. thick

and 15 ft long. The plates were sheared into 7-in. sections with forces of 8000 to 33,000 lb. The force required for cutting varied inversely with the amount of pile exposure.

Radioactive contamination from the shearing of irradiated plates of natural uranium was controlled by performing the operation in an open tank in a disassembly basin.² The radioactivity in the tank was kept at a low level by recirculating the water in the tank through a filter and an ion-exchange column. During the shearing operation the highest activity of water in the tank was $8 \times 10^{-3} \mu\text{c}/\text{cm}^3$, which was only a factor of 20 above background activity of the water in the basin. Activity of air above the tank did not increase, and the radiation level in the working area (4 ft above the water) was only 3 mrads/hr. Contamination of the shearing equipment was low enough (25 mrads/hr at 3 ft) to allow the equipment to be removed from the tank and worked upon directly.

At Atomics International, an automatic de-canner has been developed³ for the Sodium Reactor Experiment (SRE) fuel elements (2.8 per cent enriched uranium for core 1 and 7.6 per cent uranium-thorium for core 2). Fuel slugs for the SRE are contained in a stainless-steel can having a length of about 8 ft, a diameter of 1 in., and a wall thickness of 0.01 in. The cans are to be opened to release the slugs. A Carborundum wheel traverses the rod longitudinally at approximately 2 ft/min. The wheel is positioned manually to cut the can without cutting into the slugs. Its vertical position requires almost constant adjustment to compensate for wheel wear and bowing of the can. The cans are immersed in kerosene during the cutting operation in order to neutralize the NaK contained within the cans.

Equipment for mechanical disassembly, dejacketing, and recanning of spent SRE fuel has

been designed, fabricated, and installed in a shielded segmenting facility at ORNL.⁴ Remote performance testing of the equipment with unirradiated fuels showed that all operations are feasible. Irradiated fuel is expected to be processed at a rate of 250 to 500 kg of uranium per day. Mechanical processing of spent fuel was expected to begin early in 1961. Details of this work are reported in several ORNL progress reports.⁵⁻⁸

Chemical Dejacketing

Materials used for cladding (namely, aluminum, zirconium or Zircaloy, stainless steel, and Hastelloy X) may be removed by selective chemical dissolution. The fuel cores thus exposed can be dissolved by another reagent in a second step.

Removal of Zirconium and Zircaloy Jackets

Zirconium-clad or Zircaloy-clad fuel elements having oxide cores may be dejacketed by the Zirflex process. In this process the cladding is dissolved in 6M ammonium fluoride-1M ammonium nitrate.

Data from Hanford Atomic Products Operation (HAPO), reported in the July 1960 issue of *Reactor Fuel Processing*,⁹ showed that the dissolution rate of zirconium fell off by a factor of 4 as the pH increased from 5.5 to 8.8. In Zirflex decladding studies at ORNL,⁵ the average dissolution rate of Zircaloy-2 was decreased only ~10 per cent when a volume of 1.0M ammonium hydroxide (rather than water) was gradually added to the dissolvent (4.5M ammonium fluoride-0.5M ammonium nitrate) to maintain a constant level in the dissolver as the overhead condensate was withdrawn.

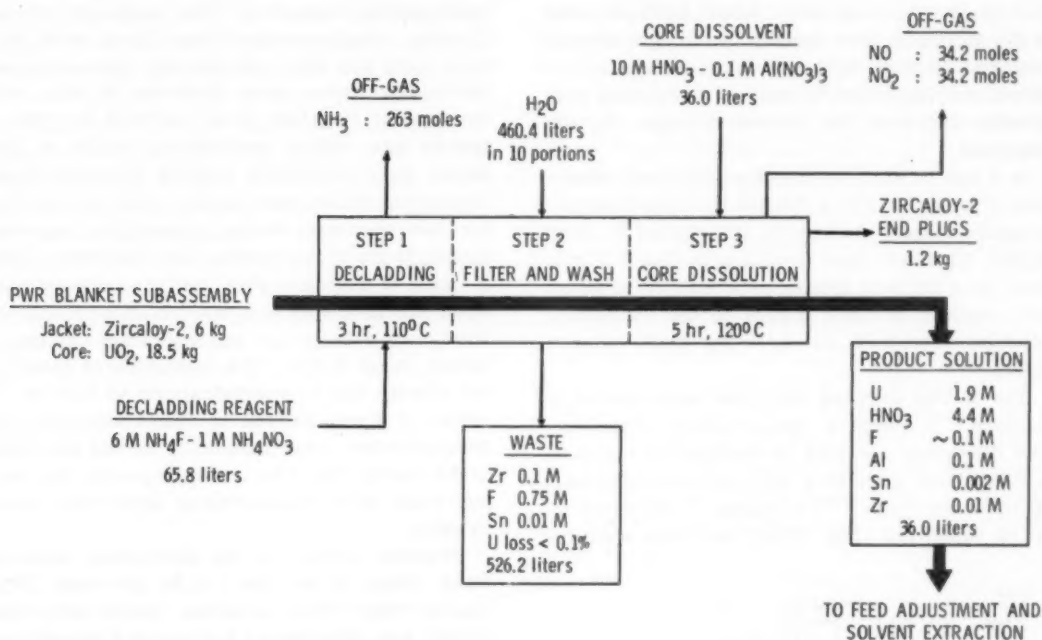
In additional Zirflex bench-scale tests of the dissolution of Zircaloy-2 in 4.5M to 6M ammonium fluoride-0.5M ammonium nitrate, runs were made to attempt to produce a dejacketing waste solution free of solids.⁶ Although low free-fluoride concentrations in the range of 0.4M to 0.8M are required to prevent precipitation of the ammonium fluozirconates, the free fluoride cannot be totally depleted if the hydrated oxides of tin and zirconium are to be held in solution. Even with complete withdrawal of the overhead condensate containing ammonium hydroxide, solids formed when the free fluoride was depleted. However, with a fluoride-

to-zirconium charge ratio of 6.5, relatively solid-free solutions containing ~0.7M zirconium were produced with both 4.5M and 6M ammonium fluoride-0.5M ammonium nitrate, with complete withdrawal or with rectification and reflux of the overhead condensate.

A summary report of laboratory-scale experiments at ORNL in the development of the Zirflex process for the Pressurized-Water Reactor (PWR) blanket fuel has recently been issued.¹⁰ The final flow sheet, shown in Fig. III-1, provides for incomplete dissolution of zirconium by a high dilution of the decladding waste solution and in the addition of aluminum nitrate to the core dissolvent.

The PWR blanket fuel element is a 27-mil-thick Zircaloy-2 tube (0.4 in. in diameter and 10.25 in. in length) filled with uranium dioxide pellets.¹⁰ A solid Zircaloy-2 end cap, containing about 10 per cent of the zirconium, is located at each end of the fuel element. Based on laboratory experiments on dissolution of PWR blanket fuel elements, the Zircaloy-2 tubing, which constitutes about 80 per cent of the zirconium, is dissolved in about 3 hr with boiling 6M ammonium fluoride-1M ammonium nitrate. The mole ratio of fluoride to total zirconium is 6, and the undissolved zirconium is present mainly as end caps. When the decladding step is finished, the solution is diluted to about 0.2M zirconium and then filtered or centrifuged. The uranium dioxide core pellets are washed with about one volume of cold water or 0.05M aluminum nitrate in several portions to remove sorbed fluoride. The wash solution is added to the decladding solution, producing a final waste solution containing 0.1M zirconium. This ensures that no $(\text{NH}_4)_3\text{ZrF}_7$ will precipitate, even if the fluoride-to-zirconium ratio in solution is 20. Soluble uranium losses are expected to be <0.1 per cent. The core pellets are dissolved in 5 hr in a volume of boiling 10M nitric acid-0.1M aluminum nitrate sufficient to produce a solution containing 1.9M uranium. The aluminum nitrate is required to inhibit corrosion by fluoride, which is carried over from the decladding operation. This product solution requires further adjustment before the uranium is recovered by solvent extraction.

When 0.75M to 1.0M ammonium nitrate is present in the decladding solution, the off-gas is essentially pure ammonia. Only about 0.05 mole of hydrogen is evolved per mole of zirconium dissolved. The off-gas from the core

Fig. III-1 Zirflex process for decladding and dissolution of PWR blanket fuel.¹⁰

dissolution is mainly nitric oxide and nitrogen dioxide.

Since the Zircaloy-2 end caps accumulate with the dissolution of successive batches of fuel, a longer decladding time and/or a separate end-cap dissolution step every three or four cycles will be required.

A correlation for the densities of Zirflex type solutions has been obtained:¹¹

$$\rho_{\text{calc.}} = (0.99710 + 0.03157m) + (0.02046 - 0.002659m)c - (0.003346 - 0.000703m)c^2 + 0.14349x + 0.49z$$

where m = moles/liter NH₄NO₃

c = moles/liter NH₄F

x = moles/liter (NH₄)₂ZrF₆

z = moles/liter UO₂(NO₃)₂

Removal of Stainless-Steel Jackets

Stainless-steel jackets may be dissolved by either the Sulfex or Darex process or electrolytically. The Sulfex process involves dissolution of the cladding in an excess of ~6M sulfuric acid. The Darex process uses dilute aqua regia for decladding (5M nitric acid-2M hydrochloric acid). After decladding by either the

Sulfex or Darex process, the core is dissolved in a solution of 13M nitric acid-0.04M sodium fluoride-0.04M aluminum nitrate.

In continuing laboratory studies at ORNL of the Darex process,^{6,7} decladding of a prototype Consolidated Edison fuel pin irradiated to about 20,000 Mwd/ton resulted in a higher uranium loss than that normally found with unirradiated fuel.⁷ The uranium loss after a 3-hr decladding in boiling 5M nitric acid-2M hydrochloric acid was 2.2 per cent; the thorium loss was 0.07 per cent.

Soluble uranium losses from uranium dioxide-thorium dioxide pellets to boiling Darex solutions increased with increasing uranium dioxide content of the pellets.⁶ After 7-hr contact with boiling Darex dissolver (5M nitric acid-2M hydrochloric acid), 0.45 and 0.65 per cent of the uranium was solubilized from pellets containing 3 and 9 per cent uranium dioxide, respectively.

In two tests made with unirradiated-uranium Darex dissolver solution, the time required to decrease the chloride concentration from 0.87M to 350 ppm was inversely proportional to the nitrogen dioxide sparging rate;⁷ the sparging rate in one case was five times that in the other

(0.4 vs. 0.077 mole/min). About 1000 per cent of the stoichiometric amount of nitrogen dioxide required to form nitrosyl chloride was introduced. An improved method of contacting may greatly decrease the excess nitrogen dioxide required.

In a test in which a prototype stainless-steel-clad Consolidated Edison thorium dioxide-uranium dioxide fuel pellet (irradiated to about 20,000 Mwd/ton) was declad in boiling 6M sulfuric acid for 3 hr (Sulfex process), the uranium and thorium soluble losses to the decladding solution were 0.06 and 0.07 per cent, respectively.⁷

The Sulfex process has also been studied at Hanford¹²⁻¹⁴ using a recirculating dissolver. The dissolver complex is designed to maintain a subcritical geometry with enriched (possibly up to 5 per cent U^{235}) uranium.¹² The recirculating dissolver (Fig. III-2) has been operated

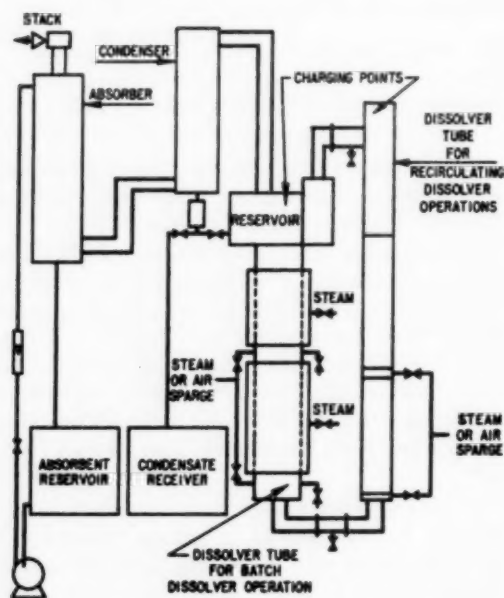


Fig. III-2 Schematic diagram of pilot vertical-tube dissolver.¹²

on a pilot scale to determine the important engineering parameters involved in the Sulfex process.

Sulfex dissolutions of stainless steels have been carried out in a series of experiments which culminated in demonstration decladdings of simulated fuel elements in a prototype-scale

recirculating dissolver. The feasibility of decladding stainless-steel-clad fuels with sulfuric acid has been conclusively demonstrated. Decladding rates were observed to vary with the type of stainless steel and with the type of sparge gas, either superheated steam or air. Steam gave improved results in every case. Decladding times were on the order of 2 to 5 hr for fuel elements having geometries approximating those of the Yankee fuel elements. Passivation of stainless steel was of no consequence when the fuel elements were coupled to carbon steel, and nitrate-ion concentration was maintained below 0.01M. The feasibility of destroying nitrate ion to concentrations <0.01M by the action of formaldehyde in Sulfex solutions was demonstrated. The possibility of the assembly braze metal (Nicrobraz 10) replacing the carbon steel as a depassivating agent was shown to exist.

Uranium losses to the decladding solutions were found to be low (<0.25 per cent) in all cases. They were, however, lower still when steam was substituted for air as a sparge gas. Hydrogen-explosion hazard was controllable by varying the acid concentration where air sparge or purge gas rates were scaled to correspond to those proposed for a production facility. The stainless-steel dissolution products are soluble to the extent of about 1M where the sulfuric acid concentration is below 5M. This solubility decreases rapidly as the acid concentration increases about 5M.

At ICPP,¹⁵⁻¹⁷ studies are continuing on the electrolytic dissolution of stainless steel. Ammonium nitrate was examined as a possible alternate electrolyte for the electrolytic dissolution of stainless steel.¹⁵ Solutions of 5M ammonium nitrate, 5M ammonium nitrate plus ammonium citrate, and 5M ammonium nitrate-0.05M nitric acid were tested. These solutions do not show promise as electrolytic media since the electrolyte apparently is decomposed in preference to the stainless-steel anode being oxidized. Although the stainless material is attacked to some extent in the basic solution, forming ferric hydroxide, the current efficiency is only approximately 30 per cent of the theoretical. Evolution of ammonia accompanies the reaction.

Removal of Hastelloy X Jackets

The Hastelloy X cladding from the Gas-Cooled Reactor Experiment (GCRE) fuel (see page 19)

dissolves at rates of 6 to 28 mg/(cm²)(min) in boiling 1M to 5M nitric acid solutions containing 4M or 5M hydrochloric acid.⁷ Solutions of 6M to 13M nitric acid or 5M nitric acid-2M hydrochloric acid-3M sulfuric acid appear suitable as reagents for leaching the uranium from the clad fuel pellets. Uranium was completely leached from the fuel pellets in 5 hr with 6M to 13M nitric acid.

In dissolution tests on Hastelloy X GCRE fuel cladding in boiling 2M nitric acid-4M hydrochloric acid, about 5 moles of hydrogen ion, 1 mole of nitrate, and 1 mole of chloride are consumed for each mole (59 g) of alloy dissolved.⁸

Dissolution

Some chemical processes perform a combined dissolution of the jacket and core. Processes reported in this section are designed for zirconium alloy, stainless-steel alloy, and uranium carbide fuels. The Alloy Reguline Chloride Oxidation (ARCO) process, in which zirconium fuel elements are dissolved in fused lead chloride, is under consideration. Proposed schemes for stainless steel include Darex-Thorex, Sulfex-Thorex, and electrolytic dissolution in nitric acid. Uranium-molybdenum fuels may be dissolved in 12M to 14M nitric acid solution containing ferric nitrate; uranium carbide fuels may be dissolved in 90 per cent nitric acid.

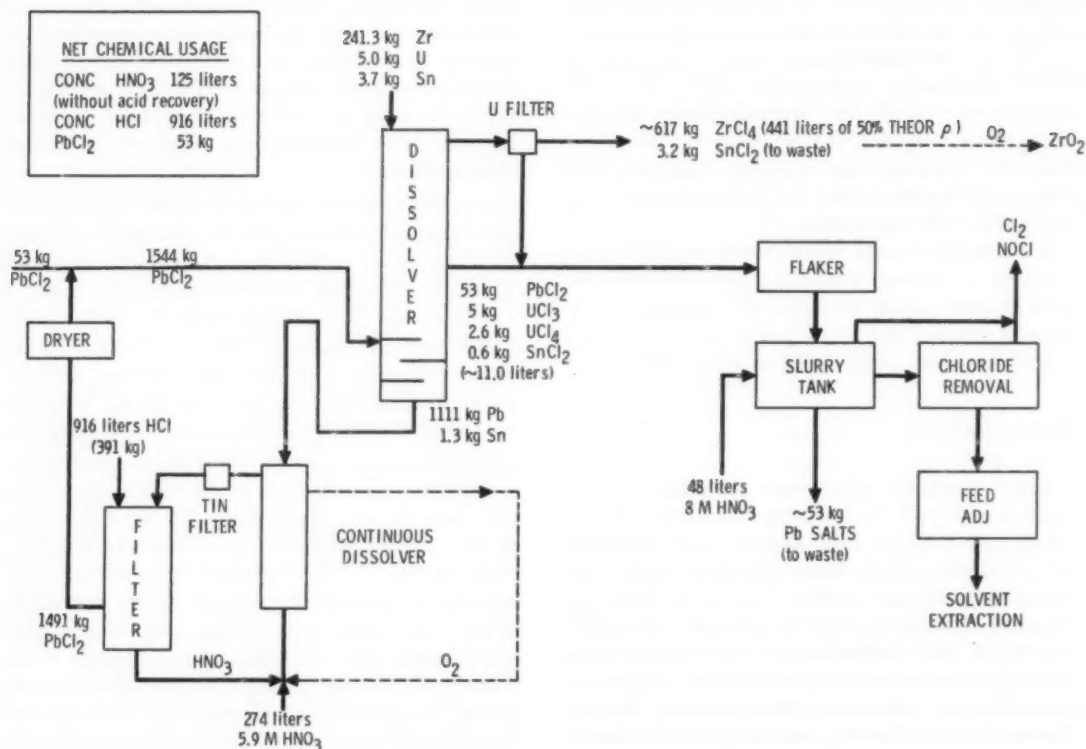
Combined Dissolution of Jacket and Core

Dissolution of Zirconium-Clad or Alloy Fuel Elements in Fused Chloride Salt. A fused-chloride-salt process under development at ICPP¹⁵⁻¹⁸ continues to look promising for the head-end treatment of zirconium and other fuel alloys. This process employs molten lead chloride as a solvent for zirconium-uranium alloys, followed by regeneration of lead chloride from the lead produced.

The dissolution of reactor fuel alloys in molten chlorides was described in a recent report.¹⁸ The basic ARCO process was investigated principally as a head-end treatment of zirconium-uranium alloys in order to provide an initial separation of uranium from zirconium. The alloy is rapidly dissolved in molten lead chloride at 520°C, at which temperature the zirconium is volatilized as the tetrachloride. Lead is precipitated as a separate metal

phase. Uranium, which is also converted to a chloride salt, may be recovered from the salt matrix by leaching with 8M nitric acid. Lead chloride may be regenerated either by dissolution of lead in nitric acid, followed by metathesis with hydrochloric acid, or by direct chlorination.

The work on the feasibility of the ARCO process may be summarized as follows:¹⁸ (1) Dissolution rates were rapid both for irradiated Zircaloy-clad fuel elements that were heavily oxidized and for unirradiated Zircaloy fuels [>300 mg/(cm²)(min) at $\sim 500^\circ\text{C}$]. Fission products of Groups I, II, and III remained principally with uranium in the salt phase, whereas ruthenium favored the lead phase; (2) uranium losses to the zirconium tetrachloride sublimate or to the metallic lead phase amounted to <0.2 per cent in one experiment; (3) <0.2 per cent of the zirconium remained in the lead chloride melt at 520°C . The addition of an equal molar amount of potassium chloride to the system to lower the dissolution temperature completely suppresses the zirconium tetrachloride volatility; (4) removal of the uranium from the salt phase by leaching was conducted with various concentrations of nitric acid, and 8M was found to be optimum. Uranium losses averaging <0.04 per cent were achieved with an 8M nitric acid leach at reflux temperatures of 107 to 108°C ; (5) several nickel alloys displayed reasonably low (4 to 7 mils/month) corrosion resistance in the lead-lead chloride system; (6) investigation of several other chlorides as media in which to perform the dissolution of zirconium indicated that none appeared to have any advantages over the lead chloride system; (7) the feasibility of dissolving other nuclear cladding materials in lead chloride was investigated. It was found that zirconium and aluminum could be dissolved simultaneously and that chromium could also be dissolved readily if potassium chloride were added to the lead chloride melt; (8) work was initiated on the application of *in situ* chlorination in fused chlorides to other metals and alloys. This concept was successfully applied to type 347 stainless steel, chromium, niobium, aluminum, and magnesium. Molybdenum also dissolved at rates that may be practical for low-alloy contents. The direct chlorination flow sheet is regarded as an advanced process flow sheet. These flow sheets are shown in Figs. III-3 and III-4.

Fig. III-3 ARCO process tentative flow sheet.¹⁸

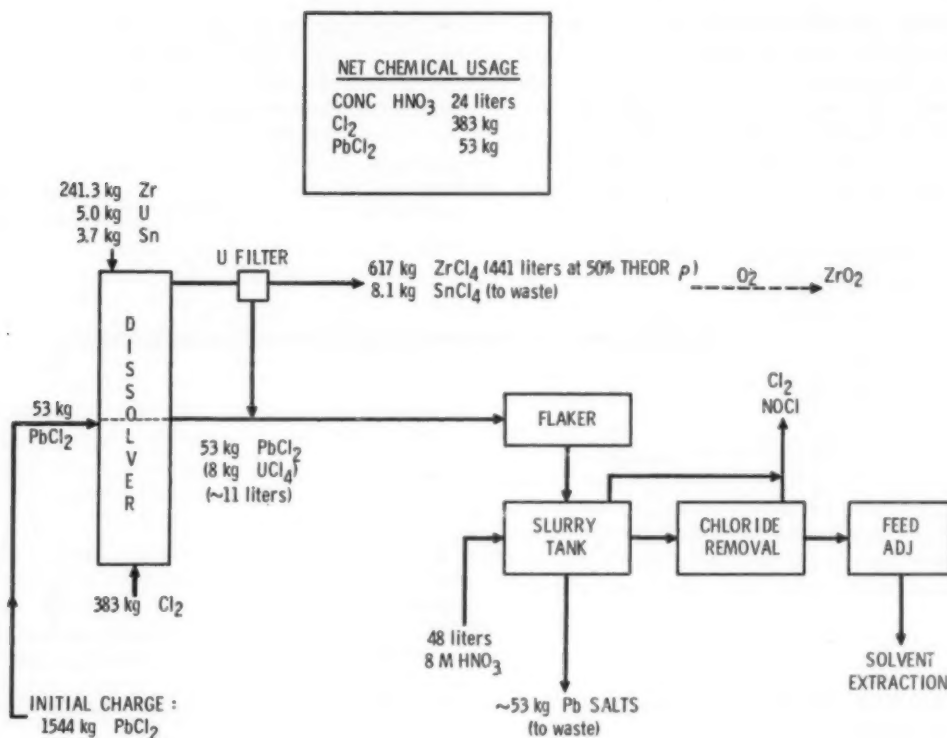
Current studies of the ARCO process at ICPP¹⁵⁻¹⁷ are investigating dissolution of uranium dioxide. Previous work has established that the oxide is insoluble in fused lead chloride at temperatures up to 750°C. Dissolution of uranium dioxide pellets in lead chloride-chlorine was investigated as a function of chlorine flow rate and temperature (520 to 800°C).¹³ With a chlorine flow of 1 g/hr, dissolution rates of up to 3.3 mg/(cm²)(min) at 800°C were achieved. At 800°C, but with higher flow rates, dissolution rates greater than 25 mg/(cm²)(min) are attainable.

In the unmodified lead chloride-chlorine system at 550°C, the average dissolution rate of uranium dioxide pellets was found to be 0.0033 mg (uranium dioxide)/(cm²)(min)/(mg chlorine)(min). In a typical experiment the passage of 0.96 g of chlorine through lead chloride for 1 hr yielded an average dissolution rate of 0.05 mg (uranium dioxide)/(cm²)(min).

Modification of melt composition is being investigated as a means of lowering ARCO

process operating temperatures.¹⁶ The lead chloride-30 mole % cadmium chloride system affords the possibility of dissolution at 400°C instead of at 500°C (pure lead chloride). In experiments completed to date, the zirconium appears to be volatilized from the new melt, while at the same time the zirconium dissolves at rates > 85 mg/(cm²)(min).

Dissolution of Zirconium-Low Uranium Alloy in Hydrofluoric-Nitric Acid Mixtures. Unirradiated zirconium-low uranium alloy and reactor-grade zirconium were successfully dissolved in boiling mixtures of hydrofluoric acid-1M nitric acid.¹⁸ Intermittent additions of concentrated hydrofluoric acid were made to the solutions in order to limit the concentration of "free" hydrofluoric acid in solution to <0.1M. Average penetration rates of 4.5 mils/hr were obtained, and the maximum off-gas rates per square foot of surface were calculated to be about 0.03 scfm. During dissolution of the zirconium-low uranium alloy, the average

Fig. III-4 ARCO process tentative flow sheet.¹⁸

composition of the off-gas was 8 per cent hydrogen, 18 per cent nitrogen, 50 per cent nitric oxide, 23 per cent nitrous oxide, and 1 per cent miscellaneous trace gases.

Electrolytic Dissolution of Zircaloy-Clad Molybdenum-Uranium Alloy. At Savannah River the electrolytic dissolution of unirradiated Detroit Edison core elements and of Zircaloy-2 was successfully demonstrated on a laboratory scale.¹⁹ Unirradiated Detroit Edison core elements (uranium-10 per cent molybdenum clad with 4 mils of zirconium) dissolved satisfactorily in 10M nitric acid when they were connected directly to the power source of an electrolytic cell with a cathode made of tantalum. Either a d-c or an a-c power supply worked satisfactorily. Less than 0.005 per cent of the total uranium was detected in the sludge formed during dissolution of the elements, after the sludge was leached for 3 hr in fresh, boiling 10M nitric acid. An average of 14 per cent of the tin and zirconium in Zircaloy-2 was dis-

solved electrolytically; the remainder of the tin and zirconium precipitated.

Stainless-Steel Fuel Elements. Several schemes have been proposed for dissolution of stainless-steel-clad uranium or uranium dioxide. These include the Darex (dilute aqua regia)-Thorex process and the Sulfex-Thorex process, which may be used for decanning and dissolution of stainless-steel-clad uranium dioxide-thorium dioxide fuels such as Consolidated Edison Thorium Reactor (CETR) fuel. Flow sheets have been developed at ORNL²⁰ for batch dissolution of CETR fuel. Figure III-5 gives a Darex-Thorex process flow sheet for CETR fuel.

The 20-mil stainless-steel cladding is dissolved in about 3 hr in sufficient boiling dilute aqua regia (5M nitric acid-2M hydrochloric acid) to yield a solution containing about 50 g of stainless steel per liter. Water used to rinse out the vessel after decladding is combined with the cladding solution to produce a waste solution

REACTOR FUEL PROCESSING

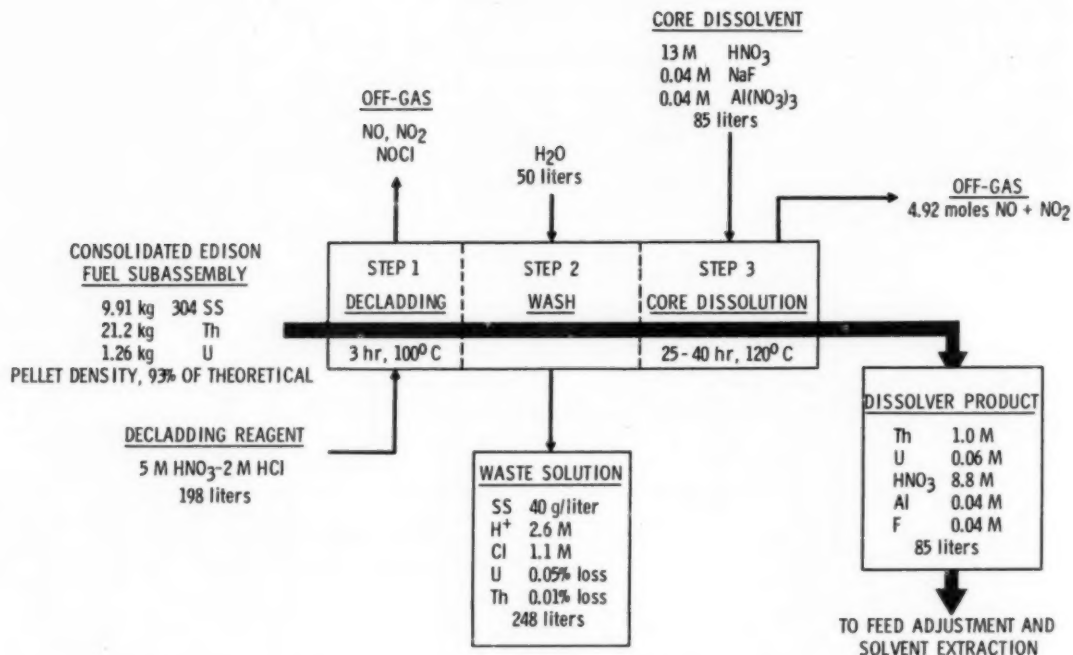


Fig. III-5 Decladding and dissolution of Consolidated Edison reactor fuel by the Darex-Thorex process.²⁰

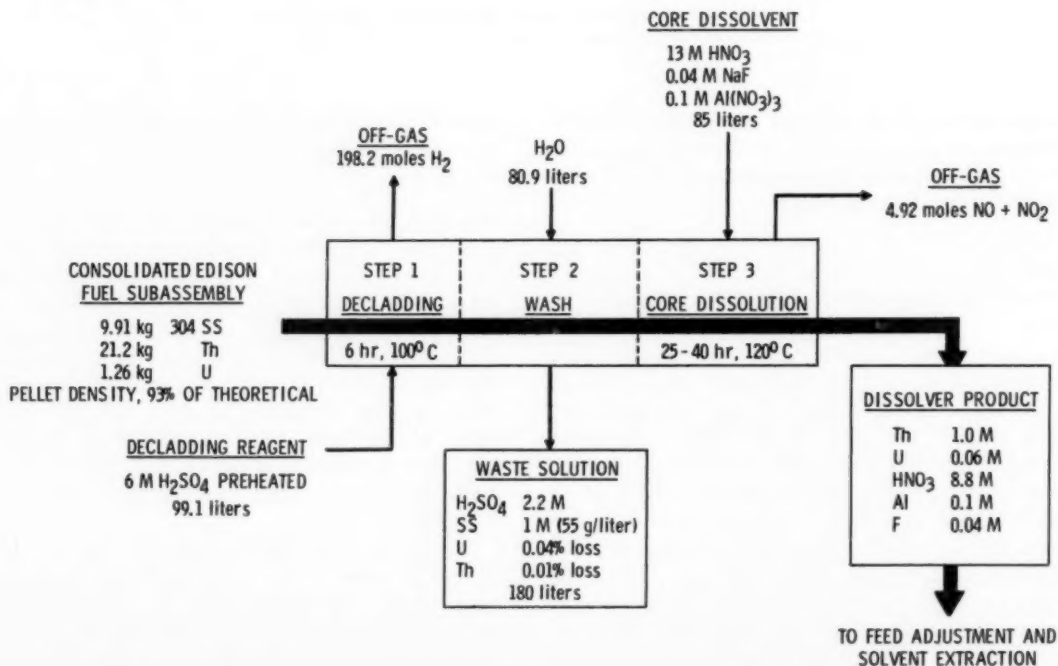


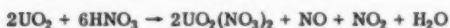
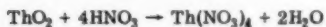
Fig. III-6 Decladding and dissolution of Consolidated Edison reactor fuel by the Sulfex-Thorex process.²⁰

containing about 40 g of stainless steel per liter. Soluble uranium losses from fuel pellets of >90 per cent of the theoretical density are expected to be <0.1 per cent; however, if losses are higher, virtually all the uranium can be recovered by contacting the cladding solution, once it is freed of chloride, with 30 per cent tributyl phosphate (TBP) in Amsco. Nitric and hydrochloric acids can be recovered by condensing the gases evolved during decladding and chloride removal.

Complete batch dissolution of the core in boiling 13M nitric acid-0.04M sodium fluoride-0.04M aluminum nitrate will probably require a minimum of 25 hr if the density of the pellets is >90 per cent of the theoretical density. A minimum of 200 per cent stoichiometric excess* of acid will be required. Repeated digestions with fresh dissolvent may decrease the time required for complete dissolution, but a more dilute product can be obtained. Under the conditions shown in the flow sheet, the product contains 1M thorium and about 9M nitric acid. Thorium and uranium may be separated and decontaminated from fission products by any of several solvent-extraction processes.

Figure III-6 shows a Sulfex-Thorex flow sheet for CETR fuel. The 20-mil stainless-steel cladding is dissolved in about 6 hr in a minimum of 200 per cent excess of boiling 6M sulfuric acid. Ideally, the reaction would be initiated with boiling 6M sulfuric acid and the solution diluted to 4M sulfate shortly thereafter. This technique results in less corrosion of the dissolver and minimizes the possibility of precipitation of stainless-steel sulfates during decladding. However, in cases where stainless steel is passive even to boiling 6M sulfuric acid, it may be necessary to initiate the reaction with 12M sulfuric acid, a technique which results in severe corrosion of Nionel. Ultimately, a waste solution containing about 55 g of stainless steel per liter will be produced. The uranium loss to the decladding solution should be <0.1 per cent if the density of the core pellets is >90 per cent of the theoretical density.

*Acid excesses are computed from the reactions



assuming the pellets to be 95 per cent ThO_2 .

After the decladding step the dissolver is washed clean of sulfate prior to core dissolution. The method of core dissolution is identical with that used after Darex decladding, except that the aluminum concentration in the dissolvent must be about 0.1M to prevent excessive corrosion of the Nionel dissolver.

Dissolution of Aluminum-Plutonium Silicon-Nickel Alloy Fuel Elements in Boiling Nitric Acid-Mercuric Nitrate Solutions. At Hanford a study of aluminum-plutonium alloy dissolution rates in nitric acid-mercuric nitrate disclosed that considerable hydrogen gas was evolved. Data for the amount of this gas evolution are available.²¹

Experiments were performed on a silicon-plutonium-aluminum alloy and on a nickel-plutonium-aluminum alloy to determine the amounts of hydrogen gas evolved when the alloys are dissolved in boiling nitric acid-mercuric nitrate solutions. The composition of the two alloys used is shown in Fig. III-7.

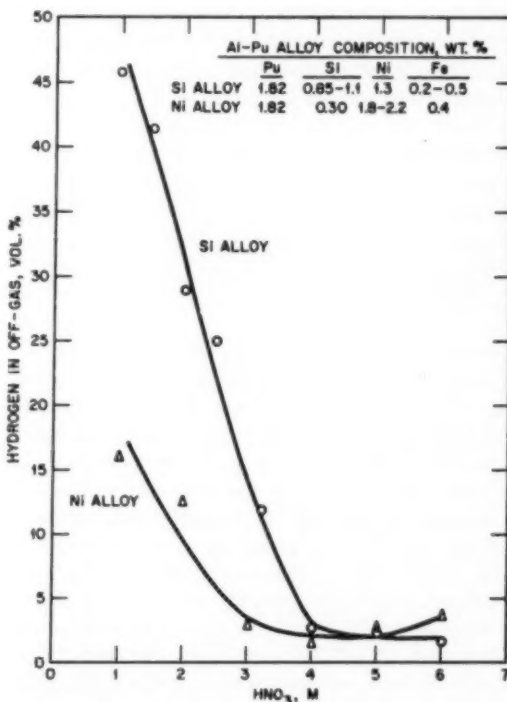


Fig. III-7 Volume per cent hydrogen in off-gas from dissolution of aluminum-plutonium alloys in 1M to 6M nitric acid-0.002M mercuric nitrate solutions.²¹

Alloy specimens were in the form of right circular cylinders $\frac{1}{2}$ in. in diameter by $\frac{1}{4}$ in. in height. In each experiment a previously unexposed alloy cylinder was activated by a 1-min exposure in boiling 1.0M nitric acid-0.002M mercuric nitrate solution. Alloy dimensions were determined, and the piece was then immersed in 500 ml of boiling 1M to 6M nitric acid-0.002M mercuric nitrate solution of the desired acidity. Dissolution was allowed to proceed for 2 min to sweep air from the reaction vessel and from the line leading to the gas burette. Then, in each case, about 90 ml of off-gas was collected in a measured time over mercury in a gas burette equipped with a leveling bulb. The gas was allowed to cool until constant volume was attained. Temperature and barometric pressure were noted. Hydrogen content of the gas was determined mass spectrometrically.

For both alloys the amount of hydrogen evolved decreased with increasing dissolvent acidity (Fig. III-7). At nitric acid concentrations above 4.0M, the off-gas from both the silicon and nickel alloys contains only about 1 to 3 vol.% hydrogen. At lower acid concentrations, more hydrogen is produced from the silicon alloy than from the nickel alloy.

Dissolution of Dejacketed Material

If fuel jackets can be removed mechanically or chemically, or if the fuel is sheared into pieces, a simpler dissolution of the core may be possible than when combined jacket-core dissolution is carried out.

Dissolution of Uranium-Molybdenum Alloys. In studies at ORNL⁵ the initial rate of dissolution of uranium-3 per cent molybdenum alloy was measured in boiling nitric acid-phosphoric acid and nitric acid-ferric nitrate solutions. In 8M and 10M nitric acid, the rate passed through a maximum when the phosphoric acid concentration was 0.25M; however, at all phosphoric acid concentrations up to 1M, the rate was acceptably high [between 60 and 300 mg/(cm²)(min)]. In 8M and 10M nitric acid solutions containing up to 1M ferric nitrate, the initial rate of dissolution varied between 140 and 310 mg/(cm²)(min). In uranium-molybdenum core dissolvents containing ferric nitrate, the corrosion rate of titanium was ≤ 0.1 mil/month over a 620-hr exposure.

The rate of dissolution of uranium-molybdenum alloys in boiling nitric acid was maximum when the molybdenum content of the alloy was 3 per cent.⁶ In 5M nitric acid, uranium and uranium-8.4 per cent molybdenum alloy dissolved at rates of 3 and 10 mg/(cm²)(min), respectively; uranium-3 per cent molybdenum alloy dissolved at a rate of about 43 mg/(cm²)(min).

In the dissolution of uranium-10 per cent molybdenum alloys in nitric acid, a molybdate precipitate forms. Data reported in a previous Review²² showed that phosphate ion prevented precipitation by forming a complex with molybdate ion. At 25°C the solubility of the molybdate precipitate resulting from the dissolution was generally highest in solutions where the nitric acid concentration⁶ was about 6M. At each nitric acid concentration, the solubility increased with increasing phosphoric acid concentration. In 6M nitric acid the solubility increased from 50 to 240 g of alloy per liter as the phosphoric acid concentration increased from zero to 1M.

Dissolution of Uranium-Graphite Fuels. Studies were made on the 90 per cent nitric acid disintegration-leach process on an unirradiated General Atomic prototype fuel specimen $2\frac{1}{4}$ in. in diameter by $\frac{1}{4}$ in. thick.⁷ The sample had a 1.5-in.-diameter inert-graphite core surrounded by a $\frac{3}{8}$ -in. active annulus containing a graphite-metal dicarbide mixture. The fuel particles were 150 μ in diameter, and the mixture contained 1.18 per cent uranium and 14.3 per cent thorium. Uranium and thorium recoveries after two room-temperature leaches with 90 per cent nitric acid were both 90 per cent. The graphite was washed with water after each leach. The reaction off-gas was a mixture of nitrogen oxides and carbon oxides. The leach solutions were dark red and contained carbon. Addition of 30 per cent hydrogen peroxide to the hot leach solution lowered the carbon concentration from 0.86 to 0.34 mg/ml. Hydrogen peroxide was more effective in decreasing the carbon content than either 70 per cent perchloric acid or 2.5N potassium permanganate.

Leaching studies of various uranium or uranium oxide-graphite fuels have shown that, in general, boiling 90 per cent nitric acid is a good leaching agent, giving >99 per cent uranium recoveries in most cases.^{6,9}

Reaction of 1 g of uranium monocarbide containing 2 to 5 per cent alpha-uranium metal with

water at 90°C in a helium atmosphere yielded 0.55 millimole of hydrogen, 3.58 millimoles of methane, 0.11 millimole of ethane, and 0.03 millimole of propane.^{5,7} The uranium product was an amorphous solid which, after dissolution in hydrochloric acid, was at least 90 per cent U(IV). No nonvolatile carbon was found, but the technique for carbon determination in hydrochloric acid is not very sensitive. Thus the principal reaction of uranium monocarbide with water at 90°C appears to be $UC + 2H_2O \rightarrow UO_2 + CH_4$.

Dissolution of Thorium Oxide-Uranium Dioxide Fuels. In dissolution tests on high-density Universal Match Company thorium dioxide-uranium dioxide pellets in boiling 15.8M nitric acid-0.01M aluminum nitrate-0.04M sodium fluoride, the study of operation with a mixed-oxide heel was continued.⁸ A 660-g batch of thorium dioxide-uranium dioxide was 95.5 per cent dissolved in 31.5 hr; a second 660-g batch of thorium dioxide-uranium dioxide was then added and reacted for 32 hr, leaving a cumulative heel of 6.5 per cent.

In tests with a modified Thorex dissolvent containing 15M nitric acid-0.1M F^- -0.2M Cr^{6+} , the dissolution rate of thorium dioxide-2.6 per cent uranium dioxide pellets of 92 per cent of the theoretical density was the same as in normal Thorex dissolvents (5.4-g pellet in ~60 hr).⁷

Dissolution of Beryllium Oxide Fuels. The fuel for the Gas-Cooled Reactor Experiment (GCRE) is Hastelloy-X-clad 70 per cent uranium dioxide-30 per cent beryllium oxide. Methods of dissolving this fuel are being sought at ORNL (see page 12 for decladding studies on this fuel). Beryllium metal dissolved in boiling 6M sodium hydroxide and 4M nitric acid-0.05M sodium fluoride; the initial rates of dissolution were 2 and 8 mg/(cm²)(min), respectively.⁵ The most effective aqueous dissolvent yet found for sintered beryllium oxide (about 95 per cent of the theoretical density) is boiling 5.8M NF_4HF_2 ; beryllium oxide dissolved at an initial rate of 1.7 mg/(cm²)(min).

Processing of beryllia containing ceramic fuels is also being studied at ICPP.¹⁷ Experiments to study the feasibility of a grind-leach flow sheet for processing beryllium-containing ceramic fuels have been initiated. Leaching uranium with nitric acid from the pulverized fuel has been examined in some scoping experi-

ments as a function of fuel particle size, nitric acid concentration, and leaching time. Leaching appeared to proceed at a practicable rate (not given), and solutions containing as high as 32 g of uranium per liter have been obtained using 3M nitric acid as the leaching solution.

Dissolution of the unground beryllia-containing fuel was effected with 12M sulfuric acid at boiling temperatures.¹⁷ A fine greenish-white residue, which has not yet been identified, remained after dissolution. A solution of 12M sulfuric acid-5M nitric acid had little effect on the fuel in a 12-hr exposure, indicating an inhibiting action of the nitric acid.

Effects of Fuel Burnup on the Dissolution Process. Reference 23 summarizes information on the effects of nuclear fuel burnup on dissolution rates and uranium losses of a few fuel types. Tentatively, the following conclusions may be stated: Burnup to the 40 per cent level has very little effect on the rate of solution of stainless steel-uranium dioxide fuel elements in solutions of the Darex type; beyond passivation, which can easily be eliminated, burnup to the 250 Mwd/ton level probably has no large effect on the rate of decladding or on the uranium losses in the Sulfex process; burnup to the 15 per cent or 4300 Mwd/ton level has little or no effect on the rate of decladding, the uranium losses, and the plutonium losses in the Zirflex process. Two other effects (namely, air oxidation of irradiated uranium dioxide and prolonged contact of this oxide with Sulfex solutions in the absence of actively dissolving stainless steel) appear to be much more serious sources of loss of uranium.

Precipitation Processes

In addition to the work at Savannah River on precipitation processes reported in the previous Review,²⁴ considerable work is being carried out at ICPP^{18-17,25} on a barium fluozirconate precipitation head-end process. Barium fluozirconate precipitation has been studied as a possible means of simultaneously removing both zirconium and fluoride from hydrofluoric acid-zirconium fluoride solutions during the processing of zirconium-uranium alloy reactor fuels. The existing zirconium process used at ICPP for high zirconium-uranium alloy fuel is burdened with excessively large waste-storage volumes. A barium fluozirconate precipitation

process has potential as a means of converting the bulk of the waste to a solid, thus allowing concentration of the highly radioactive liquid waste to a small volume for storage. By removing zirconium and fluoride in a head-end step, the extraction-column feed can be concentrated, thereby greatly increasing the uranium throughput of extraction columns.

Based on data obtained, flow sheets have been developed for head-end precipitations with barium nitrate, alkaline barium compounds, and barium fluoride-barium nitrate mixtures.²⁵ These involve dissolution in a 12.0*M* hydrofluoric acid solution containing 0.06*M* hydrogen peroxide, with the appropriate precipitating reagent added.

It is concluded that the head-end precipitation of the bulk zirconium from a portion of the fission products and all the uranium, followed by, concentration of the extraction-column feed, has considerable potential for an improved zirconium process. The small volume of barium fluozirconate waste can be dried at relatively low temperatures, compared to fluid-bed calcination, and the uranium stream can be processed in existing TBP-extraction equipment at high throughputs.

Further studies were recommended²⁵ to define the behavior of fission products, the effects of corrosion by the process streams on construction materials, and the handling and storage characteristics of the precipitates. Some of these studies have been made.¹⁵⁻¹⁷

Work has been completed characterizing fission-product distribution during the precipitation of barium fluozirconate from solutions formed by the dissolution of uranium-Zircaloy-2 in hydrofluoric acid-hydrogen peroxide systems.^{15,16} It was previously reported that strontium and cerium are carried quantitatively with the precipitate and that 20 per cent of the cesium is carried; ruthenium goes almost entirely with the filtrate. The behavior of other fission products has not been characterized; barium fluozirconate precipitates washed with 0.1*N* nitric acid carry down almost 90 per cent of the Zr⁹⁵, 80 per cent of the Y⁹⁰, and 5 per cent of the Nb⁹⁵. Fission products and uranium are washed from the precipitates with 0.1*N* nitric acid as effectively as with 0.1*N* nitric acid.

The reaction time required for the precipitation of barium fluozirconate at low temperatures is being studied for solid alkaline barium

precipitates.¹⁶ This is of particular interest because low corrosion rates were obtained at 35°C for Carpenter-20 and types 347 and 304L stainless steel in solutions from proposed barium fluozirconate flow sheets. Barium oxide is not suitable because excessive heat is produced when the reagent is added to hydrofluoric acid solutions of zirconium. Barium peroxide has an extremely slow reaction rate at 25°C. Precipitation with barium hydroxide removed 50 per cent of the zirconium in 30 to 60 min at 25°C from solutions containing a fluoride-to-zirconium mole ratio of either 5 to 1 or 6 to 1. A 5°C increase in temperature occurred at the beginning of the reaction. As shown previously, barium nitrate addition will be required to obtain adequate zirconium removal in a head-end process. The reaction time required with solid barium nitrate at 25°C is under investigation.

Alternatives to barium fluozirconate precipitation were sought as a method for removing zirconium from hydrofluoric acid process solutions. Of the methods studied, removing zirconium as a salicylate precipitate or as a hydrolysis product by boiling with paraformaldehyde and/or formic acid seemed to be the most attractive. These two methods have not been studied in more detail. The salicylic acid system is not reproducible under the conditions used; the high zirconium recovery previously reported²⁸ using salicylic acid could not be repeated in the more recent work. The best zirconium recovery, 80 per cent, was obtained by boiling dissolver solution for 6 hr with various concentrations and combinations of paraformaldehyde and/or formic acid. However, over 99 per cent of the zirconium was recovered by stirring hydrofluoric acid dissolver solutions with sodium formate at room temperature.

References

1. W. S. Delicate et al., Shearing Irradiated Uranium Plates, USAEC Report DP-185, E. I. du Pont de Nemours & Co., Inc., November 1956.
2. R. B. Olcott, Shearing Irradiated Uranium Plates, Part II, USAEC Report DP-224, E. I. du Pont de Nemours & Co., Inc., July 1957.
3. H. Schlein, Automatic De-canner—SRE Fuel Elements, USAEC Report NAA-SR-Memo-3132, Atomics International, Oct. 7, 1958.
4. C. D. Watson et al., Mechanical De-jacketing of SRE Fuel, in Proceedings of the Eighth Conference on Hot Laboratories and Equipment, San

- Francisco, California, December 13-15, 1960, USAEC Report TID-7599 (Bk. 2), pp. 337-357.
5. F. L. Culler, Chemical Technology Division Monthly Progress Report for September 1960, USAEC Report CF-60-9-113, Oak Ridge National Laboratory, Sept. 30, 1960.
 6. F. L. Culler, Chemical Technology Division Monthly Progress Report for October 1960, USAEC Report CF-60-10-118, Oak Ridge National Laboratory, Oct. 31, 1960.
 7. F. L. Culler, Chemical Technology Division Monthly Progress Report for November 1960, USAEC Report CF-60-11-118, Oak Ridge National Laboratory, Nov. 30, 1960.
 8. F. L. Culler, Chemical Technology Division Monthly Progress Report for December 1960, USAEC Report CF-60-12-94, Oak Ridge National Laboratory, Dec. 30, 1960.
 9. *Reactor Fuel Processing*, 3(3): 7-9 (July 1960).
 10. L. M. Ferris, Zirflex Process for PWR Blanket Fuel. II. Revised Flowsheets, USAEC Report ORNL-2940, Oak Ridge National Laboratory, Nov. 9, 1960.
 11. J. L. Teague and D. P. Pearson, Densities of Ammonium Fluoride - Ammonium Nitrate - Ammonium Hexafluorozirconate Solutions, USAEC Report IDO-14528, Phillips Petroleum Co., Oct. 28, 1960.
 12. F. D. Fisher, The Sulfex Process Terminal Development Report, USAEC Report HW-66439, Hanford Atomic Products Operation, Aug. 22, 1960.
 13. V. R. Cooper, Quarterly Report, Technology of Nonproduction Reactor Fuels Reprocessing, USAEC Report HW-66191, Hanford Atomic Products Operation, Aug. 8, 1960.
 14. V. R. Cooper, Quarterly Report, Technology of Nonproduction Reactor Fuels Reprocessing, USAEC Report HW-66968, Hanford Atomic Products Operation, Oct. 3, 1960.
 15. J. A. McBride, Phillips Petroleum Co., private communication, September 1960.
 16. J. A. McBride, Phillips Petroleum Co., private communication, October 1960.
 17. J. A. McBride, Phillips Petroleum Co., private communication, December 1960.
 18. E. M. Vander Wall et al., Salt-Phase Chlorination of Reactor Fuels. II. ARCO Process Definition and Scoping Studies, USAEC Report IDO-14525, Phillips Petroleum Co., Oct. 28, 1960.
 19. E. S. Occhipinti, Reprocessing of Power Reactor Fuels, Quarterly Progress Report for January 1 to April 1, 1960, USAEC Report DP-491, E. I. du Pont de Nemours & Co., Inc., October 1960.
 20. L. M. Ferris and A. H. Kibbey, Sulfex-Thorex and Darex-Thorex Processes for the Dissolution of Consolidated Edison Power Reactor Fuel: Laboratory Development, USAEC Report ORNL-2934, Oak Ridge National Laboratory, Nov. 9, 1960.
 21. W. W. Schulz and J. L. Moore, General Electric Company, Hanford Atomic Products Operation, Evolution of Hydrogen Gas During Mercury Catalyzed Nitric Acid Dissolution of Aluminum-Plutonium Alloys, private communication, Dec. 17, 1960.
 22. *Reactor Fuel Processing*, 3(2): 15-16 (April 1960).
 23. W. Davis, Jr., Effects of Fuel Burnup on the Dissolution Process, USAEC Report CF-59-3-75, Oak Ridge National Laboratory, Mar. 25, 1959.
 24. *Reactor Fuel Processing*, 4(1): 17-18 (January 1961).
 25. B. E. Paige, Barium Fluorozirconate Precipitation from Hydrofluoric Acid-Zirconium Fuel Reprocessing Solutions. Part I: Process Chemistry, USAEC Report IDO-14511, Phillips Petroleum Co., Sept. 20, 1960.
 26. C. E. Stevenson, Idaho Chemical Processing Plant Technical Progress Report for July-September 1959, USAEC Report IDO-14509, Phillips Petroleum Co., June 12, 1960.

Section IV

RESEARCH AND DEVELOPMENT ON FUEL PROCESSING

Solvent Extraction

Modifications of the Purex and Redox Processes

Plans for the interim processing of nonproduction fuels (NPF) are based wholly on either the Purex (TBP extractant) or Redox (methyl isobutyl ketone extractant) process or a combination of the two processes. In view of the facts that these fuels are irradiated to considerably higher burnups than production reactor fuels and, that, in many cases, they contain alloying elements, it has been necessary to devote considerable effort to the development of modifications of the basic processes. In general, these modifications seek to minimize radiation damage to the solvent and to provide adequate decontamination in foreign chemical environments.

In the development of processes for nonproduction fuel of high enrichment, the problems of criticality control require careful consideration. One means of control is to limit the amount of uranium in the system by reducing its TBP content, and thereby limiting the maximum uranium loading capacity of the solvent. Uranium distribution data are systematically being obtained on kerosene-diluted solvents containing 5 to 20 per cent TBP. A summary of data obtained to date covering uranium extraction from nitric acid solution with 5, 10, 15, and 20 per cent TBP in Amsco 125-82 is available. These data cover uranium concentrations in the aqueous phase from 0.1 g/liter to more than 300 g/liter.^{1,2} Batch studies of fission-product decontamination comparing 5 and 15 per cent TBP at 68 to 61 per cent uranium saturation showed that the decontamination factor dropped by a factor of 2 as the TBP concentration was increased from 5 to 15 per cent.²

The assessment of flow-sheet conditions for processing the Consolidated Edison fuel, 95 per cent thorium dioxide-5 per cent uranium dioxide, continues to be of interest. More data have been published covering the distribution of uranium and thorium between zero and 0.2M nitric acid solutions containing 100 to 200 g of thorium per liter and 30 per cent TBP in kerosene.² Flow sheets based on extraction with 10 to 40 per cent TBP were compared. Extraction with 10 and 20 per cent TBP gave the best decontamination but excessively high thorium losses. Solutions containing 30 and 40 per cent TBP gave lower decontamination but negligible thorium losses. There are certain advantages in the use of 40 per cent TBP, namely, a decreased volume of aqueous wastes, a decrease in the acid requirements for salting, and a probable increase in plant capacity by as much as 30 per cent.³ Selected data for the various acid Thorex processes are presented in Table IV-1. (Note:

Table IV-1 ACID THOREX PROCESS:
SELECTED DATA³
(Flow Ratios: Feed/Scrub/Acid/Solvent = 1/1/1/7
for All Systems)

	10% TBP*	20% TBP*	30% TBP*	40% TBP*
Feed:				
Th, g/liter	95	196	278	362
U, g/liter	5.7	11.2	16.2	21.5
H ⁺ , M	0.1	0.13	0.16	0.1
Organic product				
Th, g/liter	2.5	19.4	40	50
Thorium loss, %	77	7.6	0.08	0.005
Decontamination factor (γ):				
Ru	>3600	~2700	600	342
Zr-Nb	1600	3180	900	900
Pa	50	140	100	220

*In Amsco-diluted extractant.

Thorex decladding and dissolution flow sheets are given in Sec. III, pages 15 to 17.) Purex processing of highly irradiated plutonium alloys will probably involve extraction with TBP and neutralization of the aqueous raffinate, followed by extraction of americium and curium with TBP. The latter extraction will also remove rare earths which behave similarly to the actinides. Preliminary tests showed that distribution coefficients for cerium and europium between 30 per cent TBP and aluminum nitrate solution increased from 3.2 to 480 for europium and from 1.8 to 180 for cerium as the aluminum nitrate concentration⁴ was increased from 1M to 2M.

A National Lead Company of Ohio (NLCO) publication⁵ describes in detail a very interesting liquid-liquid extraction process for the recovery of slightly enriched (0.94 per cent U^{235}) uranium from a slurry feed. The slurry, containing about 25 per cent solids, was produced by the dissolution of slag-liner residue from the bomb reduction process. Alumina was used to complex fluoride in the slag, and, as a result, the feed solution contained about 1.5M aluminum nitrate. The most satisfactory flow sheet employed an extractant of 15 per cent TBP in kerosene and a feed slurry containing 25 to 30 g of uranium per liter, 1M nitric acid, and 1.5M aluminum nitrate.

Studies of Alternate Extractants

Interest continues to mount in a variety of organonitrogen and organophosphorus compounds aptly described as liquid ion-exchange resins. This interest stems largely from the ability of these reagents to extract uranium from a variety of acid media. At the present time, alkyl amines and alkyl phosphoric acids are in use at production facilities as extractants of uranium from ore leach liquors. In the processing of highly irradiated fuel, however, their application must await further testing, particularly with respect to radiation resistance. In addition, they must demonstrate considerable economic advantage to justify their replacement of the Purex and Redox processes. Currently, there are no firm plans to employ these alternate extractants in the processing of any reactor fuel.

In the United States the bulk of the studies of alternate extractants has been conducted at ORNL. Since 1952, ORNL has evaluated over 200 organonitrogen compounds. Screening tests

conducted during the interval 1957 through 1960 are summarized in reference 6. Each reagent was first tested for its ability to extract uranium. Satisfactory extractants were then tested for other important properties, such as diluent compatibility, aqueous solubility, and uranium selectivity. The findings of this study can be roughly classified as follows:

1. Branched chain primary amines gave good uranium extraction and phase separation.

2. Straight chain amines were poor uranium extractants. Alkyl ether amines formed permanent emulsions.

3. Branched chain secondary amines were good extractants in both kerosene and benzene, but they were unsatisfactory in chloroform diluent.

4. Straight chain secondary amines were good extractants in chloroform, but they were poorer by a factor of 10 in kerosene and benzene.

5. The tertiary amines, both straight and branched chain, were excellent extractants in kerosene, kerosene-alcohol, and benzene, but they were relatively poor in chloroform.

6. Quaternary ammonium compounds were poor extractants.

Evidence of considerable Italian and French interest in alternate extractants is apparent from current publications. Data obtained by French workers on the extraction of plutonium and fission products from nitric acid solution by 0.17M trilaurylamine (TLA) in dodecane are presented in Fig. IV-1. These findings show that the distribution coefficient for tetravalent species increased with increasing atomic number. Table IV-2 shows that, in 2M nitric acid, satisfactory separation factors are available for isolating plutonium from most actinides and from typical fission products. Other data (Fig. IV-2) show the pronounced effect of uranium on the plutonium distribution coefficient, which is reduced by a factor of 4 as the uranium concentration is increased from zero to 100 g/liter. The various extracted complexes show limited solubility in the diluent, but the solubility can be increased considerably by the addition of 5 per cent octyl alcohol. The authors conclude that TLA shows promise as an extractant for plutonium fuels, with little or no uranium present, or for plutonium-uranium fuels after the partition cycle.⁷

Additional data on long-chain tertiary amine extractants have been published by Italian

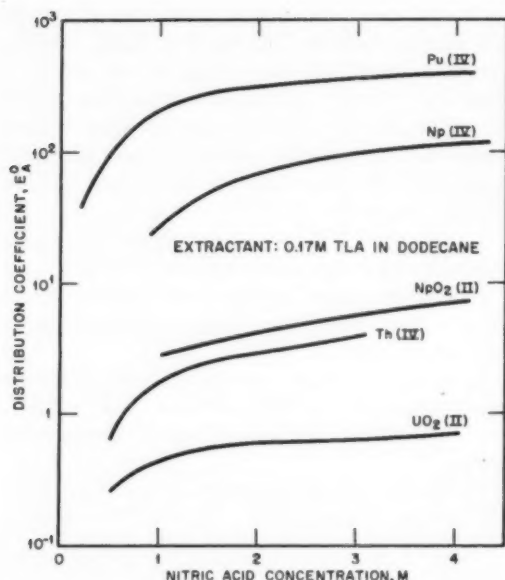


Fig. IV-1 Distribution coefficients for the extraction of several actinides by TLA.⁷

Table IV-2 SEPARATION FACTORS FOR Pu(IV) FROM VARIOUS TETRAVALENT ACTINIDES AND FISSION PRODUCTS⁷

(Extractant: 0.17M TLA in Dodecane; Aqueous Phase: 2M HNO₃)

Substance	Separation factor ($E_A^0 \text{ Pu} / E_A^0 \text{ substance}$)
Th(IV)	100
Pa(IV)	500
UO ₂ (II)	600
Np(IV)	4
NpO ₂ (I)	$>2 \times 10^4$
NpO ₂ (II)	90
Pu(III)	10^5
Am(III)	10^5
Ce(III)	10^5
Zr(IV)	10^4
Ru(IV)	$\sim 5 \times 10^3$

workers.⁸ The amines studied were tri(iso-octyl)amine (TIOA) and three commercial mixtures, Alamine 336 (General Mills), XE-204 (Rohm and Haas), and Odogen 363 (Archer and Daniel). Distribution ratios were determined for extraction with 10 per cent amine in Solvesso-100 modified with 5 per cent nonyl alcohol, for nitric acid, uranium, and various fission products obtained from Purex aqueous waste. The range of variables studied was nitric acid, zero

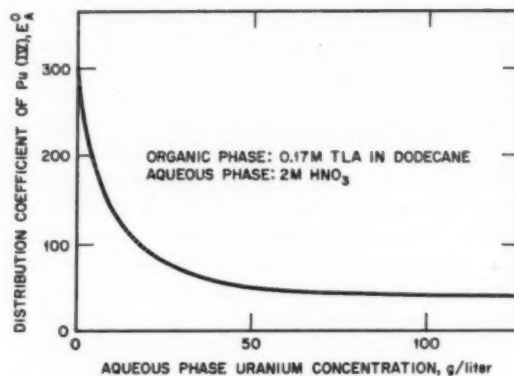


Fig. IV-2 Effect of uranium on the extraction of Pu(IV) by TLA.⁷

to 10M; uranium, zero to 1.5M; and amine concentration, 0.05M to 0.5M. In extraction from 1M nitric acid containing tracer levels of activity, decontamination factors for beta activity varied from 850 for Odogen 363 (a mixture rich in TLA) to 410 with TIOA. In comparison, the decontamination factor obtained using TBP was 137. Fission-product decontamination factors for individual fission products were in excess of 10^6 for cesium and the rare earths, 1200 for ruthenium, rhodium, and niobium, and 2.5×10^4 for zirconium. This work confirms previous findings by other investigators indicating relatively poor ruthenium decontamination by tertiary amines.⁸

In other studies, Pu(IV) isotherms, reported for plutonium recovery by extraction with 0.3M TLA and other tertiary amine, were correlated by the following empirical expression:⁹

$$E_A^0 = \approx 2500 (M_{\text{amine}} - 4M_{\text{Pu}})^2$$

Stable organic phases were noted to loadings of 15 g/liter for 0.3M amine (TLA and Alamine 336 diluted with Solvesso-100 containing 10 per cent tridecanol). Somewhat lower solubility limits were observed with Amsco-5 per cent tridecanol diluent.

In studies of organophosphorus alternate extractants, di-2-ethylhexyl phosphoric acid (D2EHPA) has received the most attention and is now employed in production facilities for the recovery of uranium from ore.¹⁰ Stripping uranium from the solvent with sodium carbonate solution has not been completely satisfactory. The principal difficulty in D2EHPA stripping is

the low solubility of its sodium salt (Na D2EHP) in kerosene.¹¹ The solubility of Na D2EHPA in diluent can be increased slightly by the addition of sodium nitrate, as shown in Table IV-3. A survey of a large number of solvents shows that some solvents provide a considerable increase in solubility, as noted in Table IV-4. A novel

Table IV-3 SOLUBILITY OF D2EHPA SODIUM SALT IN BENZENE¹¹

Aqueous-phase NaNO ₃ , M	Na D2EHP solubility, M
0.4	0.001
1.0	0.013
2.0	0.057
3.0	>0.5
6.0	>0.5

Table IV-4 SOLUBILITY OF D2EHPA SODIUM SALT IN VARIOUS DILUENTS¹¹

Diluent	Solubility, M
<i>n</i> -Butyl ether	1.0
Dibutyl carbitol	1.0
Diisobutyl	1.0
<i>sec</i> -Butyl benzene	0.002

technique has been developed on a bench scale wherein uranium is precipitated directly from the organic phase as ammonium uranyl tricarbonate (AUT).¹⁰ This process was developed primarily for ore processing. The stripping solution (0.9M to 1.6M in ammonium carbonate) is contacted with uranium-loaded D2EHPA [0.1M D2EHPA-0.05M diamylamyl phosphonate (DAAP) in kerosene]. The precipitated AUT is separated by filtration and converted directly to U₃O₈ by calcination at 300 to 500°C. This technique is also applicable to amines and other organophosphorus compounds, such as TBP and alkyl phosphonates.

D2EHPA is also an excellent extractant for Pu(IV) from nitric acid solution. Typical plutonium extraction coefficients are given in Table IV-5. Extraction coefficients for Pu(VI) varied with the square of the D2EHPA concentration and with the inverse square of the acidity. Extraction coefficients for Pu(IV) were a factor of 1000 lower than those for Pu(VI), and extraction coefficients for Pu(III) were even lower.

Work continues on the development of a process for the recovery of strontium and rare-earth activities from tartrate-complexed

Table IV-5 PLUTONIUM EXTRACTION WITH D2EHPA-KEROSENE EXTRACTANT¹¹

Extracted species	Extractant	Extractant coefficient, E_a^0
Pu(IV) in 1M HNO ₃	0.1M D2EHPA	~2500
Pu(VI) in 4M HNO ₃	0.1M D2EHPA	~10
Pu(IV) in 1M HNO ₃ and 5M NaNO ₃	0.1M D2EHPA	~3000
Pu(VI) in 4M HNO ₃	0.1M D2EHPA; 2% tridecanol	~6
Pu(VI) in 4M HNO ₃	0.1M D2EHPA; 2% tridecanol; 0.05M TOPO	~60

caustic-adjusted Purex waste by extraction with D2EHPA.¹² In the most recent tests, waste solution (1M in tartrate to prevent iron precipitation and adjusted to pH of 5.5 ± 0.5 with caustic) was treated with an extractant consisting of 0.3M D2EHPA and 0.15M TBP in Amsco 125-82. Strontium and rare earths were stripped from the extractant with 2M nitric acid, and the aqueous product was fed to a second cycle after adjustment of the pH to about 2 with caustic. Rare earths and strontium are partitioned in the second cycle by stripping strontium with 1.2M sodium nitrate and the rare earths with 2M nitric acid. Testing of this flow sheet with Ce¹⁴⁴ and Sr¹⁸⁵ tracer showed a rare-earth-to-strontium separation factor of 2.5×10^4 , a rare-earth concentration factor of 20, and a strontium concentration¹² factor of 70.

A topical report is available on the separation of transplutonium and rare-earth elements by liquid-liquid extraction.¹³ Since most of this work has been mentioned in previous Reviews, only the highlights of the process are mentioned here. The process is being developed for the recovery of Pu²⁴², Am²⁴³, and Cm²⁴⁴ from highly irradiated Pu²³⁹. Americium and curium were separated from rare earths by extraction from 10M lithium chloride-0.5M to 1.0M hydrochloric acid solution with 0.5M mono-2-ethylhexyl phosphoric acid (M2EHPA) in xylene diluent. Distribution data for the actinides and rare earths of interest are shown in Fig. IV-3. Depending on the flow rates and flow ratios employed, americium can be separated from all rare earths, or americium and curium can be separated from all rare earths except lanthanum.¹³

Some British data are available on the use of DAAP as a replacement for TBP in the Purex

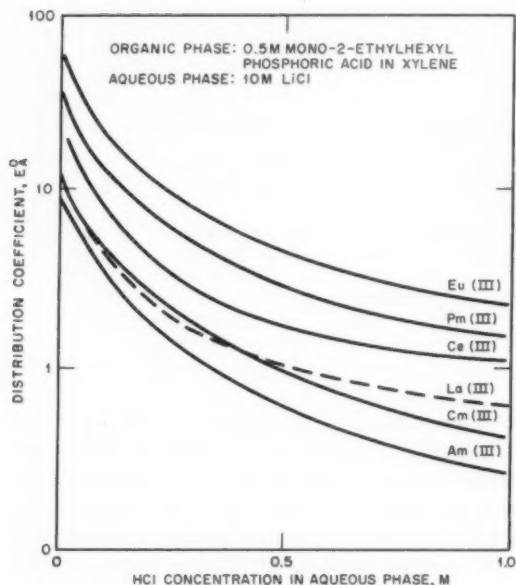


Fig. IV-3 Distribution coefficients for various rare earths in the M2EHPA and LiCl-HCl systems.¹³

process.¹⁴ The diluent used, descriptively called odorless kerosene (OK), is a carefully controlled fraction free of olefins and aromatics. Tests conducted with actual separation-plant feed solution showed DAAP to be a superior extractant for uranium and plutonium but a poor performer with respect to decontamination from gamma activity. Some representative data presented in Table IV-6 show that DAAP would not be a satisfactory replacement for TBP in the processing of irradiated fuels.¹⁴

Table IV-6 REPRESENTATIVE PARTITION DATA COMPARING DAAP AND TBP (20 VOL.% OK)¹⁴

Solvent	Uranium conc. at equilibrium in aqueous phase, g/liter	Distribution coefficient, E_a^0	
		Uranium	γ activity
DAAP	20.6	2.36	0.07
TBP	26.4	1.55	2.5×10^{-4}
DAAP	1.91	11	0.35
TBP	5.43	3.76	3.8×10^{-4}

In studies of the use of di-*sec*-butylphenyl phosphonate (D-*s*-BPP) in the Purex codecontamination cycle, erratic behavior of plutonium has been observed.¹⁵ Batch studies showed that

only by very careful feed preparation could excessive plutonium losses be avoided. The feed preparation procedure developed to ensure complete plutonium extraction by 1M D-*s*-BPP in Solvesso-100 required the addition of 0.025M to 0.05M aqueous nitrate, followed by digestion at 50°C for 1 hr.

Solvent Degradation

Degradation of process solvents as a result of chemical and radiation damage yields many products deleterious to solvent-extraction processing. Studies at Stanford Research Institute (SRI), which are reported in a semiannual report,¹⁶ are concerned with the effects of radiation in mixed solvent-extraction systems containing various combinations of acids, water, Amsco 125-82, Solvesso-100, and TBP.

Inasmuch as this work was performed under subcontract to ORNL and is reported in its monthly reports, most of the highlights have been mentioned in previous Reviews, particularly the October 1960 issue.¹⁷ Among the work not previously discussed is the destruction of nitric acid by radiation.¹⁶ The irradiation samples of TBP-Amsco equilibrated with 2M nitric acid showed that radiolytic damage to nitric acid in such systems is substantial and is temperature dependent. At temperatures of 25 to 35°C for 0.752M and 1.505M TBP, the nitric acid destroyed was 74.6 and 69 per cent, respectively, for 10^{24} ev (330 to 400 watt-hr/liter) irradiation. Under comparable conditions but at 70 to 80°C, the percentage destruction of nitric acid was 98.6 and 98.2, respectively.¹⁸

After a critical review of the radiolysis data obtained in initial studies, SRI concluded that improved methods were desirable for the quantitative determination of very small quantities of organic phosphate and phosphoric acid produced by TBP degradation. A satisfactory process was developed, based on ascending paper chromatography to separate trace quantities of dibutyl phosphate (DBP), monobutyl phosphate (MBP), and phosphoric acid followed by neutron-activation analysis. The analytical technique is capable of the quantitative determination of as little as 0.1 μ g of phosphorus.¹⁸

Certain anomalous radiolysis results were explained by a careful comparison of various lots of Amsco 125-82 used in the 1957 through 1960 studies.¹⁸ G values noted in Table IV-7 show that considerable variation in quality may

Table IV-7 VARIABILITY¹⁸ NOTED IN RADIOLYSIS OF DIFFERENT LOTS OF AMSCO 125-82

Lot	Grams of iodine absorbed per 100 g of sample	G values*		Ratio of methane to hydrogen formation
		Total gas	Double bonds (C = C)	
1		4.6		0.22
2	~1.7	2.7	3.5	
3	7.9	1.8	2.8	0.03
4	8.2	1.7	3.5	0.20

*Molecules formed per 100 ev of irradiation.

exist between different lots of Amsco 125-82. Lot 3 is noteworthy because the relatively high contamination with unsaturated components, as evidenced by the iodine number in combination with other unknown factors, apparently exerted a significant protective effect against radiation damage.¹⁸

As more experimental data become available, a mounting body of evidence is being accumulated showing diluent degradation products to be more difficult to remove from used solvent than those from TBP. Therefore considerable attention is being given to the nitroparaffin reaction products of hydrocarbon diluents and nitric acid. Nitroparaffins of the RNO₂ type apparently undergo a tautomeric shift, as noted, to an acid form that strongly complexes zirconium, niobium, and ruthenium in the organic phase.^{12, 19}



Parallel testing of TBP in Amsco 125-82 and D-s-BPP in Solvesso-100, both equilibrated with nitric acid and irradiated with Co⁶⁰, showed that nitrohydrocarbons are formed in both aliphatic and aromatic diluents. Various methods of solvent cleanup, scrubbing or absorption, netted similar results; namely, the bulk of the zirconium-niobium activity was not removed from the diluent.¹²

Infrared measurements have provided a useful technique for evaluating the quality of degraded solvent.¹¹ Amsco 125-82, thoroughly degraded by boiling in 8M nitric acid, was examined by infrared analysis. The presence of aliphatic nitrohydrocarbons was strongly indicated. When the extraction characteristics of degraded solvent were compared with those of Amsco 125-82 spiked with nitrohydrocarbons, comparable behavior was noted. These studies indicated ni-

trooctane as the probable principal degradation product responsible for the fixation of zirconium-niobium in degraded Amsco.

The over-all picture of ruthenium retention by degraded diluent is complicated by the changes in the behavior of ruthenium as the solution is aged. No difference in ruthenium extraction behavior was noted in a comparison between fresh solvent and solvent significantly altered by (1) chemical degradation of the diluent, (2) addition of TBP hydrolysis products, or (3) irradiation of the solvent.¹⁵ However, when the solvent containing ruthenium was allowed to age for several days, a radical change in ruthenium behavior was noted. Simple scrubbing techniques were no longer effective in removing ruthenium.¹⁵

During the interval Nov. 11, 1958, to Nov. 9, 1959, NLCO subjected to in-plant evaluation the use of three criteria for solvent condition as indicators of the ease of refinery operation. The three criteria were uranium retention, emulsion coalescence time, and infrared spectral analysis. The solvent used in the refinery is 33.5 per cent TBP in kerosene in the pulse columns and 22.5 per cent TBP in the mixer-settler units. Periods of relatively poor solvent conditions, readily detectable by the three criteria, could be correlated with refinery operations. The tests of solvent quality also proved that routine centrifuging of sodium carbonate washed solvent (Report NLCO-775, p. 17) was beneficial.²⁰

Russian studies²¹ treating the subject of plutonium complexing by TBP degradation products, MBP and DBP, show the complex to be of the form PuR₄:



Equilibrium constants are presented for 1M to 6M nitric acid solution of 6.15×10^3 for DBP and 1.5×10^3 for MBP on the assumption that the complex is formed as follows:



where $n = 1, 2, 3, \text{ or } 4$.

Plant and Equipment Design

and Development Operation

Dissolution Equipment. The Darex process is designed to convert stainless-steel-jacketed

fuel elements into solvent-extraction feed. The various Darex flow sheets proposed involve two steps: (1) The total dissolution of the fuel elements in a dilute mixture of nitric acid and hydrochloric acid and (2) the removal of excess chloride to prevent undue corrosion of the stainless-steel processing equipment. The findings from pilot-plant studies of the batch Darex process have been reported by Shefcik.²² A description of the dissolver pilot plant is given below.

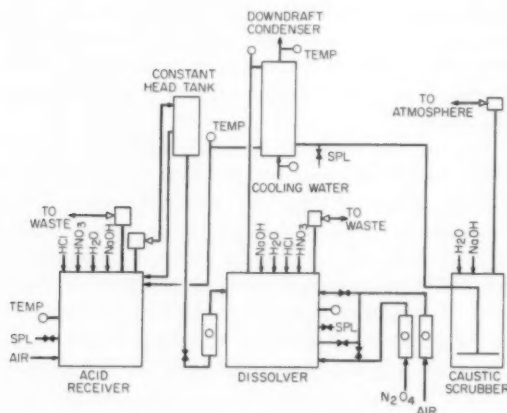


Fig. IV-4 Darex pilot plant.²²

The schematic layout of the Darex pilot-plant unit is shown in Fig. IV-4. The dissolver, acid receiver, condenser, and interconnecting lines are of commercially pure titanium. The rectangular dissolver is 15 in. wide, 54 in. long, and 45 in. high and has a working volume of about 300 liters. Water or steam circulating through a 40-ft coil of 1-in. titanium tubing is used to regulate the solution temperature. The downdraft condenser is 6 in. in diameter and 9 ft long. The cooling water flows through seven 1-in.-diameter vertical tubes inside the condenser and through 1/2-in. copper tubing coiled around the outside of the condenser. The external coil, installed to alleviate thermal stresses, was wrapped with aluminum foil prior to lagging. Fluorothene Raschig rings in the lower half of the condenser vapor passage provide a large surface area for the absorption of the oxides of nitrogen by the condensate. The noncondensable vapors pass through a titanium distributor ring submerged in a dilute caustic solution contained in a 500-liter stainless-steel tank. From the

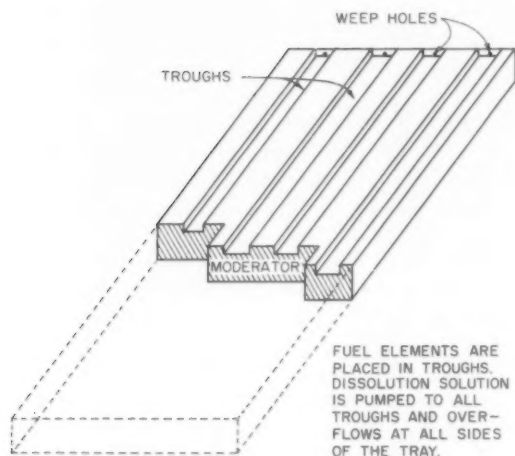
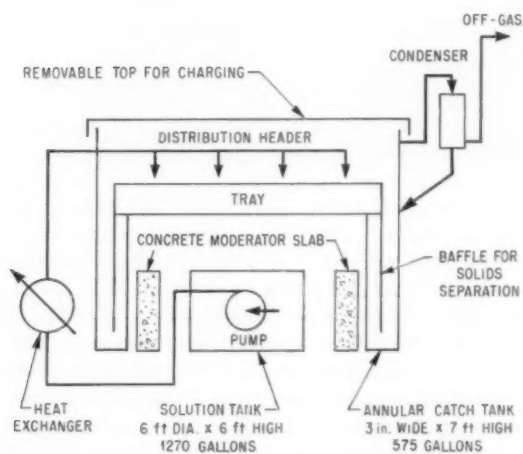
caustic scrubber, the off-gas passes through a steam exhaust jet before being discharged to the atmosphere.

The 500-liter acid receiver is used as an aqua regia makeup tank and as a condensate receiver. A titanium jet, a constant head tank, and a glass-lined rotameter are used to meter the aqua regia from the acid receiver to the dissolver. Teflon tubing and Penton (chlorinated polyether) or PVC (polyvinyl chloride) valves are used on the various samplers and in the condensate line from the condenser. Polyethylene tubing and PVC piping and valving are used in the hydrochloric acid piping system.

A fundamental problem of the Hanford NPF program is the design of a dissolver critically safe for up to 5 per cent U^{235} -enriched nonproduction fuels and having a capacity of 1 ton per day. Two basic design concepts have evolved, both of which employ a recirculating system in which the fuel elements are placed in the critically safe geometry separated from the bulk of the solution in another vessel. In one concept the fuel elements are charged to a set of geometrically safe cylinders or tubes, and solution is circulated through them. In the other concept the fuel elements are placed in a flat tray, and solution is sprayed over them. In the latter system, nuclear safety is obtained by avoiding submerged dissolution and the resulting neutron moderation by the solution. A study was carried out to evaluate the possibility of combining the best features of both these concepts into a single system. The results of this study are described and reported by McKee.²³

The basic trough-tray concept is that a number of troughs are combined into a single trough by placing them side by side in a horizontal plane and connecting the troughs together to form a large tray. Each trough is sized to be geometrically safe for a heterogeneous 5 per cent U^{235} system, and each trough is separated from the next one by a concrete moderator and neutron absorber (thin sheets of boral or cadmium) or by sufficient air space to minimize interaction. A simplified sketch of this tray is shown in Fig. IV-5.

Fuel elements may be charged to the troughs either as subassemblies or as chopped fuel. Solution is pumped from a separate vessel to the troughs and overflows back to the solution tank. A sketch of the complete system is presented in Fig. IV-6. If the trays are deep enough for complete submersion of the elements, only moderate

Fig. IV-5 Dissolver tray.²³

TOTAL SOLUTION CAPACITY, INCLUDING TROUGH ~ 2000 GALLONS

Fig. IV-6 Tray dissolver system.²³

solution distribution over the trays at three or four points along each trough is required. However, if the trays are not deep enough for complete submersion of the elements, more thorough solution distribution over the elements might be necessary and could be provided through the use of deflector plates. It is visualized that whole-element subassemblies would be strapped together into bundles for charging, using dissolvable straps, and that chopped elements would be loaded into baskets for charging.

The solution flows in a thin layer across the tray and overflows into a safe annular tank

around and below the tray. This annular tank, which is equipped with a center baffle, also serves as a solids separator. The solution overflows from the annular tank into a larger capacity solution tank. An external heat exchanger and a condenser complete the system.

The possibility of flooding the tray must be prevented since this would increase the depth of solution on the tray beyond the nuclearly safe limit. This could be done by fixing the pump position in the solution tank so that the pump would lose suction after about 100 gal of solution had been pumped to the tray if the annular tank overflows should plug. The 100 gal would not be enough to fill the annulus remaining above the overflow point. Another method to prevent tray flooding would be to supply supplementary overflows above the normal overflows from the annular tank.

Nuclear interaction between the tray and the solution tank (underneath the tray and inside the annular tank) must be minimized and can be accomplished in several ways. A 12-in.-thick slab of concrete can be placed between the tray and the solution tank or the tray can be separated from the solution tank by an air space, but the required separation appears to be too great for practical application. Another method that could be used, if the tray is 6 or 7 ft wide, would be to place the solution tank beside the tray and annular tank assembly rather than under it.

This dissolver system has the following advantages:

1. Fuel-element chopping is not required, but chopping can be used to increase capacity if desired.
2. An adequate solution surface area for vapor evolution is provided. The solution surface area is 20 to 50 times as great as that available in the capsule type dissolver. This should minimize foaming problems and permit taking maximum advantage of dissolution accelerating agents such as ferric nitrate.
3. The dissolver is safe for fuel elements enriched with up to 5 per cent U^{235} .
4. There will be no need for spray generation unless, perhaps, the unit is not designed for complete submergence of the fuel elements.
5. Only low-head recirculation is required.
6. Only a single pump or recirculating device is required.
7. The design provides easy access to the trays for visual inspection to determine if dissolution has been complete.

The operation of a vertical-tube recirculating-dissolver pilot plant for nitric acid dissolution of uranium dioxide has been reported by Smith.²⁴ The study was pointed toward the comparison of uranium dioxide dissolution rates in a batch and a recirculating dissolver and the definition of hydraulic problems associated with the recirculation of nitric acid by airlift techniques through beds of reacting uranium dioxide.

The apparatus used in these tests is shown schematically in Fig. IV-7. A 7.5-in.-ID by 15-ft-high dissolver tube was connected at the bottom to a 10-in.-ID by 8-ft-high reservoir tube

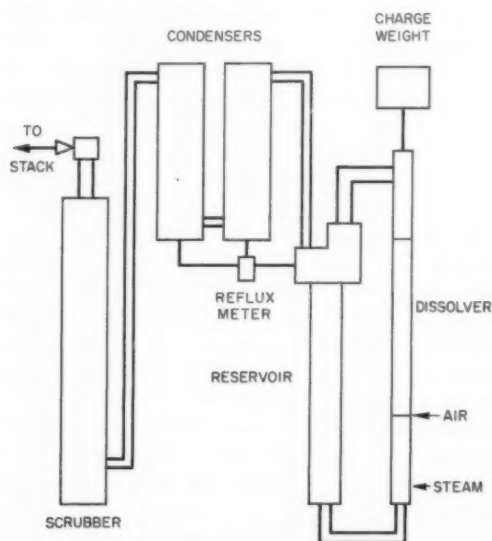


Fig. IV-7 Pilot-plant vertical-tube dissolver.²⁴

through a 4-in.-ID pipe. The dissolver tube overflow at the 12-ft level was connected to a disengaging box attached to the top of the reservoir tube. A plate that separated the disengaging box into two sections contained several orifices for liquid flow measurement and an opening at the top for off-gas passage. Two condensers and a scrubber were connected to the disengaging box for off-gas treatment. The reservoir-to-dissolver volume ratio for the unit was 1.5 to 1.

The results of tests performed were as follows:

1. Dissolution rates under recirculating conditions were essentially the same as rates predicted from batch data.

2. Air flow from an airlift ring located below the reaction bed had no apparent effect on dissolution rates for material in the size range to be encountered in the proposed nonproduction fuel processing.

3. Difficulty was encountered in the initiation of liquid flow by airlift through packed beds of uranium dioxide containing a high percentage of fines.

4. Location of the airlift sparge ring above the packed beds proved to be more reliable for initiating liquid flow than locations below the bed.

5. The air sparge required for a given liquid flow was highly dependent on the rate of gas formation from the reaction and the dissolver temperature. Air requirements for the circulation of hot dissolver solution (212°F) during reaction were a factor of about 4 less than for circulation of cold dissolver solution (70°F) (e.g., 50 vs. 14 cfm at a liquid flow rate of 11 gal/min).

6. Foaming in the dissolver was negligible.

Miscellaneous Plant Equipment. A simplified, low-speed, direct-drive agitator was constructed and tested under conditions simulating those to be encountered in both the Redox and Purex plants.²⁵ All gear-reduction drives were eliminated by using a special hollow-shafted 300-rpm electric motor, and the probability of metallic fatigue was reduced by using a 4-in.-diameter hollow shaft. The unit was evaluated with the four different shaft lengths of interest in both plants and proved to be free from critical speed difficulties. Agitation and uniform blending of the contents of a 10-ft-diameter by 10-ft-deep tank were accomplished in approximately 1 min. Durability was demonstrated by over 21,000 hr of operation of a similar agitator and by about 2500 hr of this unit. In addition, operation was vibration free, and satisfactory agitation of the process solution was obtained.

Equipment Decontamination. Reference 26 is a review of the development of decontamination procedures at Hanford for large high-unit-cost chemical processing equipment. The decontamination of several major buildings, using a technique of loosening and flushing contamination into waste-storage tanks or into a container for subsequent disposal underground, was successfully performed. Various cleaning agents were evaluated for their decontamination effectiveness and their reaction on the soil re-

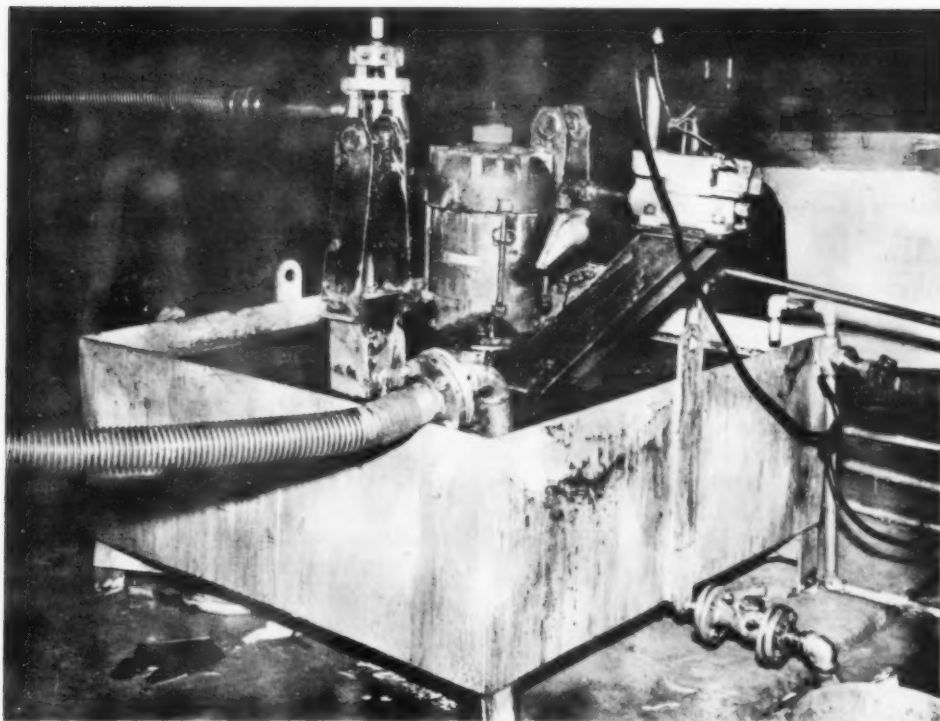


Fig. IV-8 Immersion of smaller equipment in a thimble tank containing decontaminating solution.²⁸

tention of radioactivity in the cribs used for waste disposal. The most favorable results were obtained with 1 per cent sodium citrate-5 per cent sodium hydroxide when followed by an acid flush. Versene, tartrate, and a commercial caustic cleaner were found to have an adverse effect on the crib soil for absorbing fission products. Pressure spray techniques with perchloroethylene and with inhibited 1,1,1-trichloroethane were found to be very effective for the decontamination of oily surfaces. Alkaline permanganate solutions were found to be effective for the decontamination of acid-resistant, painted concrete surfaces. Plutonium contamination levels in excess of 5×10^6 dis/min were encountered. Vacuum cleaning, repetitive scrubbing with various chemical solutions, and water mopping achieved major reductions. In some cases, levels were reduced to 100 dis/min, and, in others, from 500 to 100 dis/min. Where the remaining activity was impractical to remove, the activity was immobilized with several spray coats of paint and

then covered with a final, more wear-resistant coating.

A centralized decontamination facility for the decontamination of pumps, agitators, and small process vessels is used. The facility consists of thimble tanks (see Fig. IV-8) which permit simultaneous immersion and operation in decontaminating solutions. A typical decontamination cycle includes successive treatments with 15 to 25 per cent caustic solutions containing an oxidizing agent, a water flush, 10 to 25 per cent nitric solutions containing a reducing agent, and another water flush. Techniques other than water and chemical flushes have also been utilized. Sandblasting and ultrasonic cleaning have been evaluated and are used when they are considered economically suitable.

Where the size of the equipment makes it difficult to move, decontamination techniques for on-location use have been developed. The decontamination of an extraction column was performed by flushing the inside with hot solutions of 15 per cent nitric acid, 6 per cent

caustic-1 per cent tartrate, 5 per cent oxalic acid, and 5 per cent caustic-1.55 per cent permanganate. The outside of the column was washed down by overflowing the vessel. The vessel is then moved to a prepared work area within the building for further decontamination and repair.

Considerable savings in equipment costs have been achieved through the use of equipment decontamination techniques. The cost of decontaminating, inspecting, and repairing equipment having an original cost of \$293,629 was \$71,343 for a period of two years. A list of this equipment is given in the report.²⁶ The savings of \$222,287 is regarded as being conservative since disposal of equipment that has failed involves a substantial burial cost, and the original costs listed do not reflect increased replacement costs.

Plant Operation. The Power-Reactor Fuel-Processing Pilot Plant located at ORNL was designed to process spent reactor fuel originating in various AEC-owned research reactors.

A report issued recently²⁷ deals with a four-month period of pilot-plant operation in which a total of 46.8 metric tons of spent Brookhaven National Laboratory (BNL) reactor fuel was processed to recover 22.6 kg of plutonium and 46.6 tons of depleted uranium.

The objectives of this program were as follows:

1. To demonstrate a satisfactory chemical flow sheet for the continuous recovery of plutonium and uranium from spent reactor fuel
2. To conduct a sustained run in pilot-plant equipment which would demonstrate, under conditions of equilibrium operation, the capabilities of the pilot-plant facility
3. To separate and recover for return to normal production channels ~22.6 kg of plutonium contained in 46.8 metric tons of spent BNL reactor fuel
4. To demonstrate and evaluate the effects of operating the extraction columns with the organic phase continuous
5. To continue the development of satisfactory accountability measurement procedures

The fuel processed had been irradiated to an average of 470 Mwd/ton and had decayed for 600 to 650 days at the time of processing. The aluminum-canned fuel pieces had been mechanically sheared into 4-in. lengths at the reactor site and were transported to ORNL by truck.

The fuel pieces in most cases arrived with the residual sheath of aluminum intact; however, attack by canal water on the exposed uranium metal rods during storage resulted in some fragmentation of the uranium with the generation of finely divided material that settled to the storage-canal floor. The sediment (canal sludge) was not processed.

The fuel was fed to a continuous dissolver at approximately 400 kg/day, along with 8M nitric acid that was added continuously. A flow sheet for the dissolver and feed makeup system is shown in Fig. IV-9. To establish equilibrium

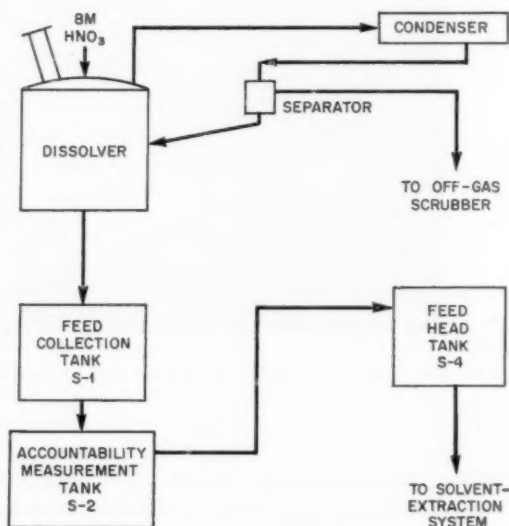


Fig. IV-9 Dissolver and feed makeup system.²⁷

on startup, approximately 200 fuel pieces were charged to the dissolver, and 8M nitric acid was added slowly while establishing the pot temperature at about 110°C (reflux condition). The rate of acid addition was carefully regulated to avoid pressurizing the dissolver. Acid addition was continued, along with the simultaneous addition of fuel pieces, until the uranium concentration of the dissolver solution approached 350 g/liter (indicated by the specific gravity and confirmed later by solution analysis), at which level the withdrawal of dissolver solution was begun. By this time a total of approximately 1000 kg of uranium metal had been added, and the solution volume in the dissolver was approximately 1100 liters. Equilibrium conditions were usually reached in about

24 hr; afterward the acid-addition rate was controlled automatically by the solution level, which was maintained in the dissolver at about the 1100-liter volume, and the metal-addition rate was adjusted to approximately 400 kg of uranium per day (14 to 15 fuel pieces per hour). At equilibrium an undissolved metal heel of approximately 700 kg of uranium was present in the dissolver. Dissolver-solution withdrawal was continuous and was maintained at a rate equivalent to approximately 400 kg of uranium per day. The dissolver solution was pumped by an underground pipeline to the feed collection tank (S-1). At intervals, sufficient 13M nitric acid was added to the collection tank to adjust the acid concentration to approximately 1.5M, and approximately 1000-liter batches were transferred to the accountability measurement tank (S-2), where the adjusted feed solution was carefully mixed and sampled and the volume was determined. Approximately 1000-liter batches of the solution were transferred to the feed head tank (S-4). After each transfer, the residual solution (heel) remaining in S-2 was sparged and sampled and the volume was determined. From these measurements, plant input was determined. The feed solution was continuously processed according to a Purex codecontamination flow sheet using 30 per cent TBP in kerosene as extractant. The flow sheet included coextraction, costripping, and evaporation of the uranium and plutonium in a codecontamination cycle. The reconstituted uranium-plutonium stream was further processed in a partitioning cycle that separated the two products, each of which was then processed in separate extraction-strip solvent-extraction cycles. The final uranium solvent-extraction product stream was passed through a silica-gel bed and evaporated to approximately 400 g/liter. The plutonium product from the final plutonium solvent-extraction cycle was passed through a bed of cation-exchange resin for concentration and further decontamination. The sorbed plutonium was eluted from the resin bed with 5.7M nitric acid at an average concentration of 46.4 g/liter and packaged for shipment in 15-liter 5.7-in. polyethylene bottles supported with 6-in. schedule-10 pipe. Wastes were monitored for uranium and plutonium before discharge to the radioactive-waste storage facilities. A total of 2.4×10^5 liters of high-level waste containing 4.2×10^5 curies of activity were generated; the total of all wastes was 1.9×10^6 liters.

Measured losses totaled 1.3 and 0.8 per cent for uranium and plutonium, respectively. The material balances across the plant were 100.9 and 102.7 per cent for uranium and plutonium, respectively; the program balances (i.e., the recovery values found in the plant operation vs. the theoretical values) were 98.2 and 92.0 per cent. The program balances reflect the effect of the storage-canal sludge resulting from fragmented and fractured fuel pieces that were not processed.

Gross gamma-decontamination factors averaging 9.1×10^4 and 1.2×10^6 , respectively, were demonstrated for the recovered uranium and plutonium products. Decontamination factors for uranium were a factor of 2 lower than the program average when the codecontamination-cycle extraction column was operated with the aqueous phase continuous, but they were a factor of 1.1 higher than the average when the organic phase was continuous. Uranium product recovered during aqueous-continuous operation exceeded radiation specifications by a factor of 2 to 10, but the uranium met these specifications in all respects during organic-continuous operation. Uranium-plutonium separation factors averaged 5.6×10^4 .

Development of accountability measurements and procedures continued throughout the program as a part of the over-all accountability measurement program. The limits of error associated with measurement of plant input during the program were determined to be ± 1.8 per cent for uranium and ± 1.2 per cent for plutonium.

Ion-Exchange Processes

Plutonium Processing by Ion Exchange

A Hanford report²⁸ describes a two-cycle anion-exchange process for the recovery of highly purified and decontaminated plutonium from nitric acid solutions of uranium fuels. It was determined that (1) plutonium can be adequately separated from uranium fuels; (2) two cycles of anion exchange, incorporating fluoride washing, will give complete decontamination of plutonium from fission products in the Plutonium Recycle Test Reactor (PRTR) fuels; and (3) the stability of Permutit SK resin toward chemical and radiation attack, coupled with its good absorption and elution rates, makes it the resin of choice for PRTR fuel processing. The

general flow sheet for this process was given in a previous Review.²⁹

Durham and Aikin³⁰ report data on concentration and purification of plutonium solutions using Dowex 50 ion-exchange resin. Equilibrium experiments using Dowex 50 ion-exchange resin and nitric acid solutions of Pu^{3+} , UO_2^{2+} , and Fe^{2+} cations have yielded values for the absorption affinities for these ions. Trivalent plutonium was found to be far more strongly absorbed than UO_2^{2+} and Fe^{2+} . Their data led to the following conclusions:

1. By absorbing solutions containing about 200 mg of trivalent plutonium per liter in 1N nitric acid onto a Dowex 50 resin column, a 50-fold concentration increase can be obtained on eluting with 6N nitric acid; about 20 per cent of the plutonium originally absorbed is left on the column.
2. A decontamination factor of 2.8×10^3 for uranium and 5 for beta-gamma was obtained using a plutonium solution from a standard run.
3. The amount of plutonium taken up by a given column can be estimated, once the feed analysis is known, by using the equilibrium constant measured in equilibrium experiments.

Recovery and Purification

of Transuranium Elements

Studies of ion-exchange methods of separating actinide and lanthanide group elements were continued at ORNL³¹ along with separation processes for transplutonium elements. In the ion-exchange method, the effects of lithium nitrate loading vs. aluminum nitrate loading, resin particle size, and column temperature were investigated. More column gassing and greater pressure drop occurred with aluminum nitrate than with lithium nitrate. Iron, however, was more readily removed in the aluminum system (99 per cent vs. 70 per cent) than in the lithium system. Temperature appeared important. At 85°C, cerium removal in seven column volumes of 10M lithium chloride was >99.9 per cent, compared to 93.5 per cent at 65°C. The resin particle size appreciably affected the separation, e.g., 100- to 200-mesh resin gave >99.9 per cent vs. 92.1 per cent cerium removal for 50- to 100-mesh resin with seven column volumes of 10M lithium chloride at 85°C. In seven column volumes of 10M lithium chloride, no americium should be removed.

Miscellaneous Ion-Exchange Studies

Ion-Exchange Purification of Reactor Cooling Water. In the past few years, ion-exchange resins have been used extensively to purify water. These resins function by removing the impurities from the influent and replacing them with water. This purification is quite often required to minimize scale formation, corrosion, and solids deposition in industrial equipment. Water purification is especially important in the case of recirculating-water-cooled nuclear reactors. In such reactors, any impurities in the coolant are continually transported through a nuclear flux region and become radioactive. This process increases the background radiation level in the external recirculation system and thus restricts accessibility and hinders contact maintenance. A multiple-unit deionization system is generally used to produce the high-quality water required for recirculating-water-cooled reactors. The system may consist of a duplex arrangement (cation exchanger followed by an anion exchanger) followed by a mixed-bed (mixed cation and anion exchangers) unit or by a series arrangement of duplex units.

A series of tests was performed to evaluate the operating characteristics of a duplex deionization system under high-flow-rate conditions.³² The cation resin used was Amberlite XE-77, the anion resin was Amberlite XE-78. Tests were run at liquid flow rates corresponding to 10, 25, 50, and 75 gal/min per square foot of cross-sectional area. Several conclusions can be drawn from the results obtained during the test series:

1. High-flow-rate operations are feasible with duplex deionization systems. Velocities as high as 75 gal/min per square foot of cross-sectional area cause only slight exchange capacity losses.
2. The effluent breakthrough curves are well defined even at the highest flow rates tested.
3. The pressure drop through the resin beds increases quite rapidly with increasing fluid velocity. The anion-bed pressure drop per unit bed depth is greater than the corresponding cation-bed pressure drop. This variation increases with increasing fluid velocity.
4. Severe capacity losses may result if channeling occurs in the resin bed. Proper design of the liquid distribution and collection systems will be imperative in high-flow-rate deionization systems.

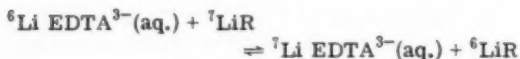
5. There was no evidence of excessive bead fracturing in samples exposed to three complete exhaustion-regeneration cycles at 75 gal/min per square foot of cross-sectional area. Bead fracturing may become important after several cycles, however.

Lithium Isotope Separation by Ion Exchange. Studies of the influence of various parameters on separation factors for lithium isotopes are being made at ORNL³³ in several ion-exchange systems. Determinations have been made in ethylenediamine tetraacetate systems, in a formate system, and on ion exchangers containing phosphorus in the active sites.

An anion complex with lithium (Li EDTA^{3-}) is formed with ethylenediamine tetraacetic acid (EDTA) at pH 10 to 11. Lithium isotope-exchange studies were made in the following systems:



where R is an anion exchanger, Dowex 1 X-10;



where R represents cation exchangers, Dowex 50 X-2 and 50 X-8;



where R is a cation exchanger containing iminodiacetate sites, Dowex chelating resin A-1.

For the Dowex 1 and the Dowex 50 X-2 experiments, the eluants were 0.25M K EDTA. For the Dowex 50 X-8 experiment, the eluant was 0.1M K EDTA. When NH_4 EDTA solutions were used for eluants, two peaks were observed in the elution curve, indicating the presence of two LiNH_4 EDTA complexes. These two peaks were eliminated by using K EDTA as the eluting solution. For the experiment where the EDTA type sites (iminodiacetate) were on the resin, 0.25M NH_4Cl was used as an eluant. In these EDTA systems, ${}^7\text{Li}$ concentrates on the resin; in all other known systems involving lithium ions on ion-exchange materials, ${}^6\text{Li}$ concentrates on the resin.

The effect of formate anion in cation-exchange systems has now been studied. Formate ion is a strong proton acceptor. It was chosen for study because it might have increased the sepa-

ration factor (α) as a result of localized hydrolysis of the lithium ion. However, the α was the same as that found for other potassium salt systems that do not affect the lithium ion species:

Anion	Formate
Resin	Dowex 50 X-16
Mesh size	-200 +400
Column dimensions (ID \times length), mm	21.5 \times 920
Flow rate, cm/sec	1.52×10^{-3}
No. of theoretical plates	600
α	1.0028

Ion-Exchange Properties of Hydrated Oxides.

The anion- and cation-exchange properties of hydrated Zr(IV) oxide, U(VI) oxide, and Zr(VI) oxide were examined.³⁴ Cation exchangers prepared from acidic oxides (e.g., zirconium phosphate, tungstate, or molybdate) when largely in hydrogen form were found to have remarkable selectivity for the various alkali metals (lithium, sodium, potassium, rubidium, and cesium). Alkali metals may also be separated from rare earths with zirconium dioxide.

Volatility Processes

The volatility of uranium and plutonium hexafluorides has been proposed as a basis for processing various types of irradiated fuels. Liquid-phase fused-salt processes are being considered for application to the recovery of uranium from molten-salt reactor fuel and from zirconium-uranium alloy fuel. Solid phase-gas phase fluorination processes have also been proposed for application to zirconium-uranium alloy fuel and to uranium dioxide fuels. Fluidization techniques are employed in these dry halogenation processes to enhance process control. In this review, results are summarized of fused-salt pilot-plant experience and of initial engineering-scale studies of the dry halogenation processes.

Fused-Salt Processes

In the fused-salt process for recovery of uranium-matrix fuel being developed at Argonne National Laboratory (ANL) and ORNL, the alloy is dissolved in the fused salt at 600 to 700°C with a hydrogen fluoride sparge, and then the uranium in the salt is volatilized as the hexa-

fluoride in a fluorine sparge. A pilot-plant-scale graphite-lined dissolver-hydrofluorinator has been developed at ANL for the first step to avoid corrosion incurred in metal systems. Dissolution of a synthetic element of Zircaloy-2 in salt containing equilibrium amounts of alloying constituents (tin, iron, chromium, nickel, and uranium fluorides) was 90 per cent complete in 10.7 hr and 99 per cent complete in 13.4 hr. This dissolution proceeded at a rate one-half as fast as that for pure zirconium in sodium fluoride-zirconium fluoride salt containing only uranium. Of the various alloy constituents present in the salt as fluorides, only the concentration of nickel was reduced by the dissolution. Substantial salt carryover in the dissolver off-gas was encountered during these runs, the major portion being retained in the sodium fluoride pellet bed and all the remainder on the porous carbon filters.³⁵

No chemical attack of salt on graphite components was revealed in an examination following disassembly. In a freezing and remelting test, extensive damage to graphite downlines was incurred. Such damage could be minimized or eliminated by suitable design and operation procedures.³⁵

The amount of salt holdup in the lampblack insulation layer between the graphite lining and the nickel shell was found to be approximately 30 lb. This salt was found, as expected, as a consequence of the porosity of the graphite (type ATL) used. The dissolver utilized a frozen-wall principle of fused-salt containment in order to prevent fused-salt contact of the outer metal shell. By surrounding the graphite crucible with a 1½-in. layer of tamped lampblack insulation, the penetrating fused salt would cool and solidify before contacting the outer metal shell, from which heat was removed by normal air convection. In this way, vapor containment was provided by the metal shell, which was protected from salt corrosion by the lampblack layer. It is possible to reduce the amount of such salt holdup by using an impregnated, less porous graphite.³⁵

The Fused-Salt Fluoride-Volatility Pilot Plant at ORNL was operated to study the recovery and decontamination of uranium as hexafluoride from molten-salt reactor fuels. Engineering experience and operating techniques have been compiled for reference.³⁶ The flow sheet for the operations is shown in Fig. IV-10. This report gives a detailed evaluation of the pilot plant as

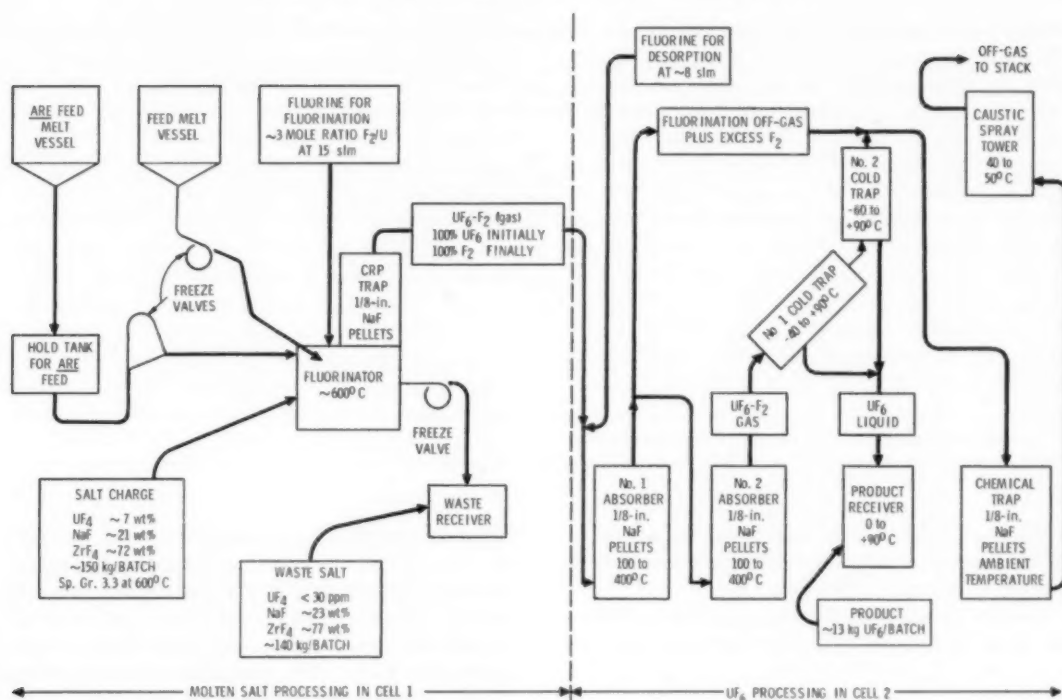
it was operated from 1956 to 1958. The several component difficulties cited concerned line plugging, sampling, and other operational problems. It was considered that such difficulties can be minimized or eliminated by improved design. This report is particularly valuable because of its objective treatment of operational difficulties, although the report is now somewhat out of date.

Direct Fluorination Processes

A direct fluorination recovery process for uranium dioxide reactor fuels is under study at ANL. The dense pelleted fuel material was shown to be capable of fluorination at practical rates. Pilot-plant-scale work has been directed toward means of controlling the reaction and removing the large amount of heat involved. The use of an inert fluidized material to cover and fill the void spaces of a nonfluidized packed bed of pellets has some of the advantages of fluidization for solid-gas reactions, particularly the removal of heat.³⁵

In experiments to date, results indicate that temperature control at higher fluorination rates (and hence rates of reaction) is limited by heat transfer from the bed to the reactor wall. In order to evaluate the heat-transfer mechanism, a series of heat-transfer tests in a mockup system was made. Representative average heat-transfer coefficients from the surfaces of heated, nonfluidized pellets in a packed bed to fluidized material in the voids were found to be over five times that for the packing without a fluid bed. These data confirm the potential advantage of fluidization for reaction control and are helpful in predicting practically achievable heat-transfer rates. These rates depend also on caking tendencies, on the range of variation of heat-transfer coefficients for individual pellets in a bed, and on the effective over-all heat transfer from the center of the bed to the reactor walls.

In the over-all fuel-recovery process, a de-cladding operation is required prior to pellet fluorination. Decladding of pellets in Zircaloy-2 tubing with a hydrogen chloride-hydrogen fluoride gas mixture was demonstrated in two initial runs. Caking of the fluid bed in this operation was found for tubes packed to nearly maximum closeness in the reactor, but caking was not appreciable for tube packing of one-half the

Fig. IV-10 Flow sheet for ORNL Fused-Salt Fluoride-Volatility Pilot Plant.³⁸

maximum. The pellets themselves showed very little attack in this operation.

Application of the direct fluorination process to recovery of uranium from fuels consisting of enriched uranium alloyed with Zircaloy has also been studied at ANL.³⁵ The process involves conversion of the metal to fluoride salts, followed by fluorination of the salts to volatilize uranium. A two-zone reaction scheme for the first step is being investigated. This scheme involves contact of the uranium-zirconium alloy with anhydrous hydrogen chloride diluted with nitrogen in the lower portion of the reactor and conversion of the volatile zirconium tetrachloride to the solid tetrafluoride in the upper zone by contact with hydrogen fluoride. Also, the uranium trichloride is probably converted to the tetrafluoride.

Proper operation of the two-zone system was shown to require a baffle between the zones to prevent gas back-mixing. Tests were made on two types of baffles, a punched plate ($\frac{1}{8}$ -in.-diameter holes, staggered spacing, $\frac{3}{16}$ -in. centers, 40 per cent open) and a 60° cone with a 1.5-in.-diameter opening. Both baffles were of

stainless steel and were installed horizontally at approximately the center of the fluidized bed. The test procedure consisted in fluidizing the bed in a 6-in.-diameter reactor with a hydrogen chloride-nitrogen mixture; admitting hydrogen fluoride gas above the baffle plate; and then, by sampling and analysis, determining the concentration of hydrogen fluoride at some distance below the baffle.

Results indicated that substantial reduction of back-mixing was achieved with either type of baffle. The ratio of hydrogen fluoride in the sample to that at the inlet was about a factor of 10 lower for each of the experiments with baffles than for the case in which no baffle was used. This was true at hydrogen fluoride rates of 0.24 and 2.4 scfm.

The cone baffle was used to demonstrate the feasibility of the two-zone reaction scheme and to form a fluidizable product for use in subsequent fluorination studies of uranium recovery as the hexafluoride. Three multiple-plate synthetic fuel assemblies (1.5 wt.% uranium-zirconium alloy) were reacted in the baffled two-zone fluid-bed reactor. The results of these

Table IV-8 SUMMARY OF HYDROCHLORINATION-HYDROFLUORINATION RUNS FOR THE TWO-ZONE PROCESS

(Equipment: 6-In.-Diameter Inconel Reactor; Specimen: 1.5 Wt.% U-Zr, 10-Plate Subassembly; Bed: 18 Kg of 60- to 325-Mesh Calcium Fluoride; Baffle: Stainless-Steel Cone with 1.5-In.-Diameter Opening; Inlet Superficial Gas Velocity: 0.36 Ft/Sec; HF/HCl Mole Ratio: 0.5 to 1.6)

HCl concentration, vol. %	Bed temp., °C	HF/HCl mole ratio	Run duration, hr	Fuel-element weight, g		Weight loss per hour, * %
				Initial	Final	
19	390	1.6	4.5	1533†	1230	2.9
60	380	0.9	6.3	1485	485	10.7
60	390	1.0	3.5	1230	617	14.2
60	400	1.0	4.0	617	144	19.2
60	425	1.0	6.0	2063†	1077	8.0
86	360	0.5	1.8	2000	1485	14.3
89	360	0.6	4.7	1077	250	16.4
88	385	0.6	4.8	3360†	2000	8.4

*The initial unit area of the charge varies from run to run.

†A new charge of metal was used in these runs. Remaining runs were made with the residual unreacted metal as the charge.

preliminary tests are summarized in Table IV-8. Approximately 90 per cent of the elements reacted in periods of about 12 hr.

Results obtained on fluorination of solid product from the above two-zone hydrofluorination

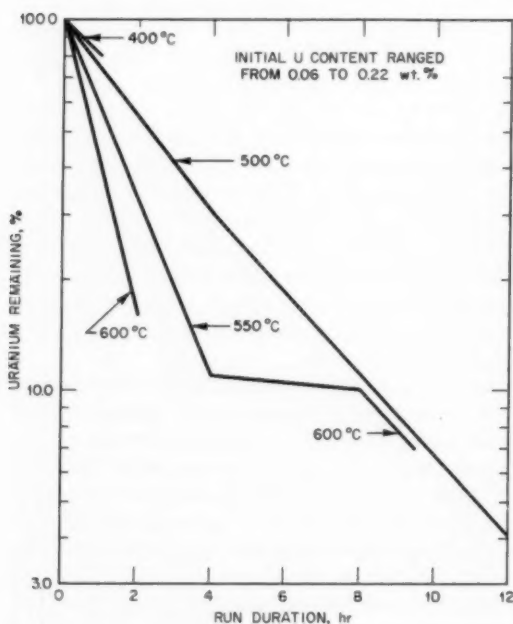


Fig. IV-11 Uranium removal during fluorination of zirconium-uranium fluorides.³⁵

are reported in Fig. IV-11. Temperature appears to have a strong effect (i.e., increased temperature gives greater initial uranium-

removal rates), but the results are not clear as far as ultimate removal efficiency. The effect of time is illustrated by the set of runs made at 500°C, where repeated 4-hr fluorinations continued to show uranium removal (up to 96 per cent) after 12 hr. The residual uranium content of this material was only 0.006 per cent. However, at 550°C a plateau was noted in which the rate of uranium removal leveled off during the second 4-hr period. A slight additional removal (to 93 per cent) was effected by a 1.5-hr fluorination of this residue at 600°C. The rate of uranium removal at 600°C was high, about 84 per cent in 2 hr. However, it is not yet known whether the removal would continue at this rate for longer fluorination periods. Similar removal (~84 per cent) was achieved at 600°C using material of two different starting uranium concentrations, 0.06 and 0.30 per cent, indicating no concentration effect in this range.

The peculiar behavior observed in the runs made at 550°C needs some clarification. Fluorination experiments are therefore planned in laboratory-scale equipment to determine the effects of time and temperature more completely.

Pyrometallurgical Processes

Simple processes capable of handling short-cooled fuels are under development at several atomic energy sites. The common goal of these developmental programs is the reduction of processing costs. Pyrometallurgical processes are among those being developed. These are processes in which metallic fuels are retained

in the metallic state or those in which the metallic state results as an intrinsic part of the process, e.g., electrochemical processes. Economic advantages accrue through avoidance of expensive chemical conversions and through the ability to handle short-cooled fuels, and thus reducing fuel inventories. These advantages are partially offset by the necessity of remote fuel fabrication which results from the relatively low, but adequate, removal of fission products provided by these processes.

Processes having these same characteristics are under development for ceramic fuels. Although those processes are pyrochemical rather than pyrometallurgical, they are included in this section on the basis of similarity.

Melt Refining

A direct-cycle fuel-processing plant using pyrometallurgical procedures is being constructed as part of ANL's Experimental Breeder Reactor No. 2 (EBR-II) project. Melt refining, liquid-metal extraction, and processes involving fractional crystallization from liquid-metal systems are methods being examined for the recovery and purification of EBR-II fuels. The first process to be employed in this facility will be melt refining, which involves simply (1) melting the discharged fuel in a zirconia crucible that is stabilized with calcium oxide and (2) maintaining the material in a molten state at 1400°C for a period of several hours to allow certain purification reactions to occur. Fission products such as xenon, krypton, cesium, and iodine either are released as gases or are vaporized from the melt. Other fission products such as the rare earths, barium, and strontium are removed by selective oxidation at the crucible walls. Separation of purified uranium is effected by pouring off the molten metal.

The construction of the EBR-II fuel-cycle facility is approximately 70 per cent complete.³⁷ An adjacent laboratory and service building has been completed and is being occupied. Various major equipment items are now being installed in the facility. These include the manipulators, cranes, and the 5-ft-thick cell windows.

A rather interesting problem was encountered with the 1000-watt fluorescent mercury-vapor lamps that had been specified for use within the high radiation fields of the processing facility.³⁸ The lamps, originally tested and found satisfac-

tory for use in high radiation environments, were made with a soft lime glass envelope. Recently the major manufacturers of these lamps changed from soft glass envelopes to weather-resistant borosilicate glass envelopes. Although the borosilicate glass envelopes are undoubtedly superior for industrial use, they darken rapidly in a radiation field. This contrasts with the performance of soft glass envelopes, which maintain a high light output even after radiation exposures of 10^9 rads (Table IV-9). A manufacturer has agreed to make a special run of lamps with soft glass envelopes for use in the EBR-II facility.

Table IV-9 PERFORMANCE UNDER GAMMA IRRADIATION OF MERCURY FLUORESCENT LAMPS WITH SOFT AND HARD GLASS ENVELOPES³⁷

Cumulative gamma exposure, rads (water)	Light output, % of original intensity	
	Soft lime glass envelope	Hard borosilicate glass envelope
0	100	100
1×10^6	98	87
1×10^7	98	34
1×10^8	97	29
5×10^8	97	18.5
1×10^9	84	*

*Test previously terminated.

An inverted cup molded from Fiberfrax* ceramic fibers has been found to be an efficient collector of condensable materials vaporized during a melt-refining operation.³⁷ The Fiberfrax cup is placed over the zirconia crucible in the melt-refining furnace. Tests carried out with sodium have indicated at least 95 per cent retention of the sodium by the Fiberfrax cup. Sodium was chosen as the test material because of its presence on fuel pins. This results from its use as a heat-transfer bond between the fuel pin and an enclosing stainless-steel can. Fiberfrax has also been found to be an efficient collector of iodine; and, presumably, it will trap cesium, which is also vaporized from the melt. The fume trap is shown in Fig. IV-12 with the furnace in a partly tilted position to indicate the manner in which the fume trap is rotated out of position during a pouring operation. This photograph, taken with the bell jar cover of the melting equipment removed, also indicates other

*An alumina-silica composition manufactured by The Carborundum Company.

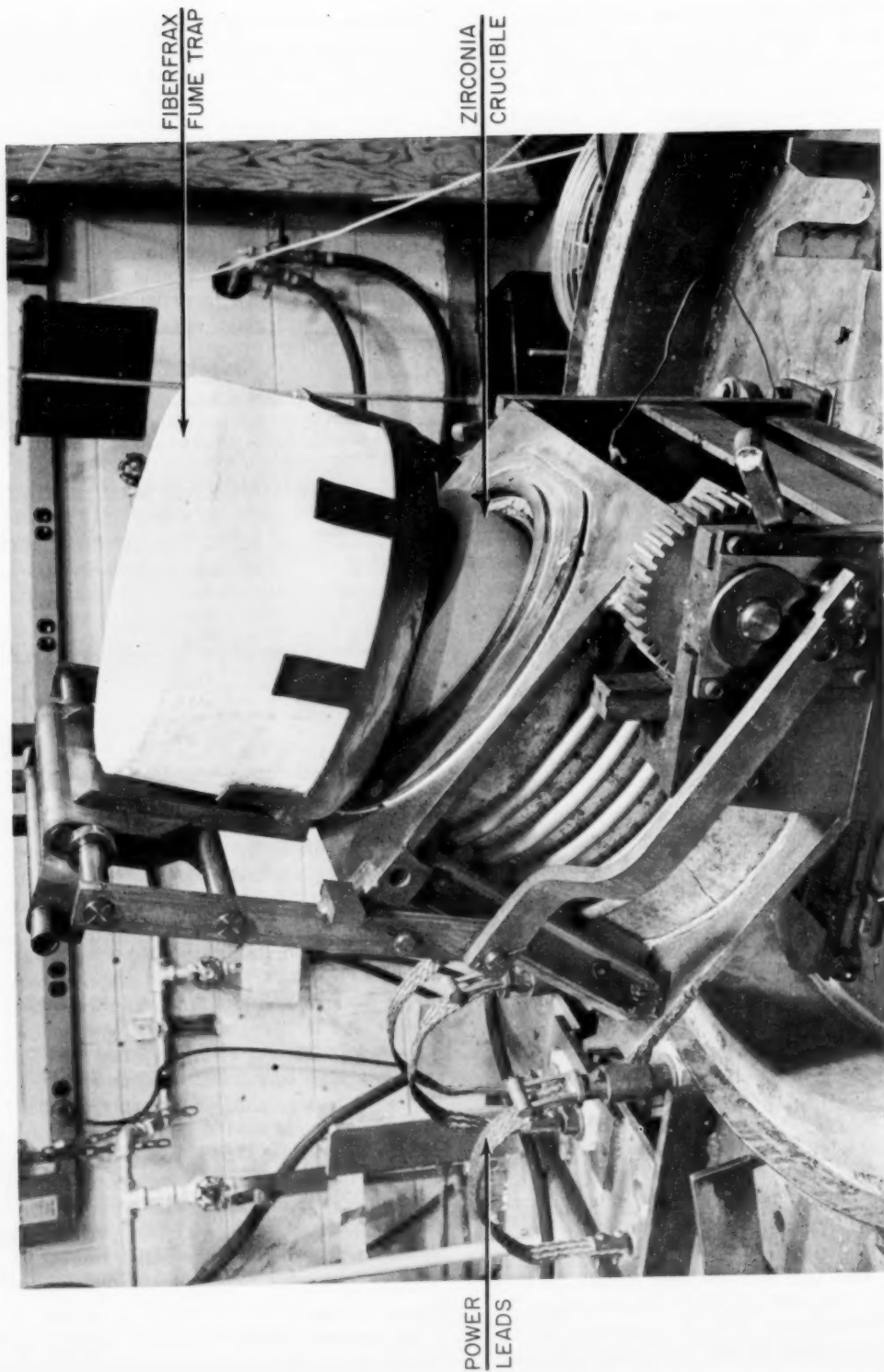


Fig. IV-12 Melt-refining furnace.³¹

components of a melt-refining unit, such as the induction coils; the rack and pinion gear by which pouring is accomplished; the zirconia crucible; and, in the background, the electrical power jumpers, which may be easily disconnected for removal of the entire furnace.

Various other material tests and progress in the development of other components have been reported.³⁷ These include, for example, irradiation tests of various lubricating greases and other insulating or structural materials and the development and design of periscopes, air locks, and manipulators. Reference 39 discusses the manipulator design developed by General Mills, Inc., according to specifications outlined by Argonne. The manipulator, which has a capacity of 750 lb, has been designed with radiation-protection or radiation-resistant components for sustained operation within a very dry inert-argon atmosphere and in a radiation field of 10^4 to 10^6 r/hr. The design permits remote replacement of critical components or of the entire manipulator. The manipulator is normally operated with five basic motions, which generally suffice for equipment operation, but an articulated arm can be attached remotely which adds grip rotation, elbow, and shoulder movements to its basic motions. A prototype manipulator has operated successfully under an extensive testing program in a full-scale mockup facility.

In the EBR-II facility the atmosphere is argon which may contain up to 5 per cent nitrogen. The extent of nitridation of the fuel alloy during times of exposure to this atmosphere is therefore of interest. One of the most likely opportunities for nitridation occurs in the decladding and subsequent handling of the fuel pins prior to melt refining. Further studies have been reported³⁷ on the reaction of uranium and uranium-alloy pins with nitrogen in an argon atmosphere. The reaction follows a parabolic rate law, and the rate constants are approximately the same for uranium and the uranium-fissium alloy. Figure IV-13 shows the variation of rate constants with temperature. Reaction rates are approximately doubled by the presence of metallic sodium coatings on the pins. Activation energies for the reaction are about 15 kcal/mole and are not affected significantly by either the presence of sodium or of the alloying constituents in fissium.

A report has also been issued on a study of the nitridation of crucible skulls remaining in the crucible after a melt-refining operation.³⁸

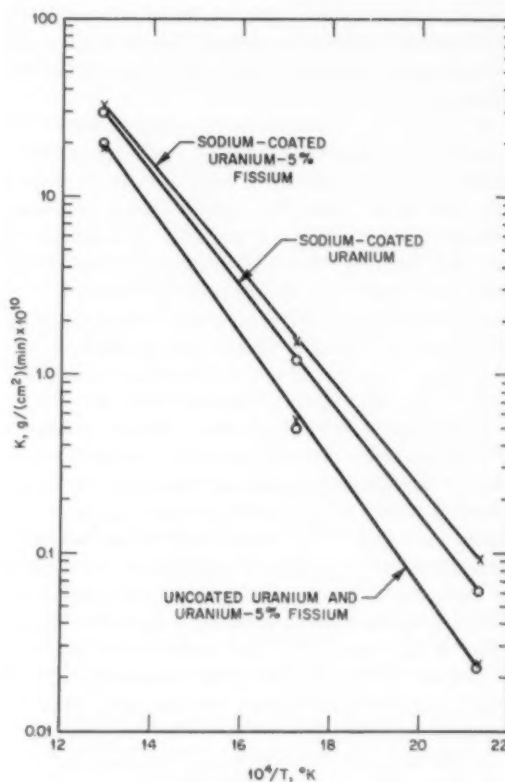


Fig. IV-13 Variation of parabolic rate constants with temperature for uranium and uranium-5 per cent fissium pins.³⁷

Because of fission-product decay heating, the temperature of such skulls may reach $400^\circ C$ or higher. In this temperature range, low-pressure nitrogen (8 to 76 mm Hg) was found to react readily with melt-refining skulls to form nonstoichiometric U_2N_3 . The skull was pulverized and loosened from the wall by the reaction. The product was very pyrophoric in air, and it appears that the conversion of nitride to oxide can, if desired, be readily effected.

A second series of articles on the melt-refining process was published in the January 1961 issue of *Nuclear Science and Engineering*. The first series appeared in the December 1959 issue. The subjects treated in the second series are the following:

1. Behavior of plutonium in the melt-refining process.⁴⁰ A uranium-20 per cent plutonium-10 per cent fissium alloy, a fuel alloy contemplated for future testing in the EBR-II reactor, may be satisfactorily processed by melt refin-

ing. A slight preferential loss of plutonium in the skull fraction was found, but this does not significantly diminish the applicability of the process.

2. *Evolution of xenon and krypton during melt refining.*⁴¹ Over 99 per cent removal of noble gases is predicted for a melt-refining operation. In this work the gases were released promptly on melting of uranium irradiated to 0.1 at.% burnup. This observation differs from that described in the preceding Review,⁴² in which noble-gas evolution from a fissium alloy irradiated to 0.6 at.% burnup was found to begin at around 700°C and to be essentially complete by the time the melting point is reached.

3. *Behavior of rare earths, yttrium, barium, strontium, and cesium in the melt-refining process.*⁴³ Virtually quantitative removal of these elements from uranium is provided by melt refining at 1400°C in calcia-stabilized zirconia crucibles, cesium by volatilization, the others by reaction at the crucible walls with oxide ions contributed by the zirconia and subsequent deposition along the walls. The reaction for removal of cerium is first order. The removal of cerium was considerably faster in zirconia than in magnesia crucibles.

4. *Sorption and retention of sodium and cesium vapor on stationary beds at elevated temperatures.*⁴⁴ A number of surface-active materials (e.g., Molecular Sieves,* activated charcoal, and activated alumina) proved to be effective at temperatures up to 800°C for trapping cesium and sodium, which are vaporized during melt refining. The capacity of the tested materials under various conditions is discussed, and equipment designs are suggested.

5. *Behavior of zirconium in melt refining.*⁴⁵ Zirconium removal is not effected by a normal melt-refining operation. However, appreciable removal (about 50 per cent) can be effected by carbide scavenging. The introduction of zirconium into uranium-cerium melts through the use of zirconia crucibles was found to be negligible.

6. *Behavior of iodine in melt refining.*⁴⁶ Melt refining of synthetic EBR-II fuel alloys in stabilized zirconia crucibles at 1400°C for 3 hr resulted in almost complete volatilization of iodine, primarily as iodides of metals present

as minor constituents of the crucible. No evidence was found for vaporization as free iodine.

7. *Behavior of ruthenium, molybdenum, palladium, rhodium, technetium, antimony, cadmium, and tellurium in melt refining.*⁴⁷ Ruthenium, molybdenum, palladium, rhodium, technetium, and antimony are not removed from the bulk metal during melt refining. Cadmium is removed by vaporization. Tellurium is removed by a proposed mechanism involving the formation of a stable compound with cerium.

The removal of fission products from molten plutonium alloys by liquation (floatation of insolubles) and slagging is one of the subjects⁴⁸ discussed in a recently issued book, *Extractive and Physical Metallurgy of Plutonium and Its Alloys*.⁴⁹ The information has previously been given in earlier issues of *Reactor Fuel Processing*.⁵⁰ The above book on the metallurgy of plutonium consists of 14 papers that treat various aspects of metal preparation, purification, chemistry, and alloying behavior. An annotated bibliography of 233 references, divided by subject matter into seven sections, is included.

A patent has been issued on a method of protecting tantalum crucibles from reaction with molten uranium.⁵¹ The protection is provided by a tantalum monoboride layer formed on the tantalum.

Studies have been reported on the rate of reaction of highly irradiated uranium with air, carbon dioxide, and steam and on the simultaneous release of fission products.⁵² The relative tendency of these reactants to promote fission-product release was in the order: air > carbon dioxide > steam. Highly irradiated uranium was more reactive than nonirradiated uranium, probably because of defects in the oxide coating produced by fission products. Complete oxidation or melting released large quantities of the rare gases, iodine, and tellurium, and, to a lesser extent, ruthenium, cesium, and strontium, the extent depending on the magnitude of self-heating.

Processing of Ceramic Fuels. The "salt-cycle" process is under development at Hanford for processing uranium dioxide fuels. The process involves dissolution of uranium oxide in a sodium chloride-potassium chloride eutectic by the action of chlorine to produce uranyl chloride, followed by electrolytic reduction to uranium dioxide. Recently, efforts have been concentrated⁵³⁻⁵⁵ on: (1) evaluating lower melting

*Sodium or other alumina silicates manufactured by Linde Company, a Division of Union Carbide Corporation.

chloride systems which might permit operation at lower temperatures and thus reduce the corrosive attack on various container materials, (2) the electrolytic production of pilot-plant quantities of uranium dioxide, and (3) preparations for demonstration of the salt-cycle process with irradiated material.⁵⁵

The most attractive alternate to the sodium chloride-potassium chloride eutectic (melting point 660°C) is a sodium chloride-lead chloride eutectic system (melting point 411°C).⁵⁴ Electrolyses at 450 to 500°C have given good adherent deposits of uranium oxide, having lead and potassium concentrations of about 200 ppm. The principal disadvantage of the lead chloride system has been the low solubility of lead chloride in aqueous systems, which has made the removal of salt from the dendritic uranium oxide deposits difficult. As in the case of the sodium chloride-potassium chloride system, the addition of a small percentage of thallous chloride increased the rate of U_3O_8 dissolution (by a factor of 6 for the lead salt system).⁵⁵ The uranium dioxide subsequently produced on electrolysis had 500 ppm lead, 500 ppm potassium, and 20 ppm thallium. Efforts to sublime salt from the oxide were unsuccessful.

In the pilot-plant electrolysis unit, about 90 lb of uranium dioxide has been produced⁵³ since July 1960. Typical analyses of oxide produced from a starting material of uranyl chloride monohydrate dissolved in the sodium chloride-potassium chloride eutectic are 30 ppm chloride, 65 ppm sodium, 80 ppm potassium, 150 ppm carbon, and an oxygen-to-uranium ratio of 2.015. The uranium oxide is deposited in continuous sheets up to 4 mm thick. Next to the cathode exists a fine crystalline layer 10 to 50 μ thick, followed by a 1.5-mm-thick randomly oriented layer of larger crystals, and then by a 2.5-mm-thick columnar deposit of large crystals. The outer formation is considered to be the most desirable. Run times of the pilot-plant unit have been limited by depletion of the salt and by buildup of tetravalent uranium by side reactions.

A low-decontamination process for oxide fuels involving oxidation-reduction cycles with air and hydrogen is being studied at Atomics International. Although the primary goals of this process are reenrichment and refabrication, some decontamination from cerium, ruthenium, tellurium, iodine, and the rare gases is expected. Remote equipment to process and refab-

ricate high-burnup fuels is under construction.⁵⁶ The scope of this project includes decladding, processing, refabrication of pellets, loading of capsules, and reirradiation through several complete cycles.

Through three oxidation-reduction cycles on material irradiated up to 7000 Mwd per ton of uranium, no significant fission-product decontamination was observed for any element except ruthenium, for which a maximum decontamination factor of 2 was found.⁵⁶ This low decontamination is believed to be the result of low processing temperatures (oxidation at 200°C and reduction at 600°C).

One run has been reported⁵⁷ with irradiated uranium dioxide powder in which the removal of ruthenium was investigated over the temperature range from 300 to 1000°C. The procedure involved heating to the desired temperature, admitting oxygen for about 15 min, sampling the oxide, flushing with argon, and heating to a new temperature for repetition of the procedure. The results given in Table IV-10 indicate that most of the ruthenium removal occurs at temperatures above about 600°C.

Table IV-10 RUTHENIUM DECONTAMINATION FROM IRRADIATED UO_2 BY REACTION WITH OXYGEN TO 1000°C⁵⁷

Temp., °C	Decontamination factor (cumulative)
309	1.1
408	1.2
517	1.2
628	1.3
739	2.6
850	4.3
1000	6.5

Significant increases in the rate of removal of uranium dioxide from stainless-steel tubes have been achieved by piercing the cladding at several points.⁵⁸ Results performed on 1/4-in.-diameter 3-ft sections have indicated nearly complete removal of the oxide in times of <10 hr at temperatures up to 600°C. In a nonvibrated setup a 1/4-in.-diameter 8-in.-long tube containing uranium dioxide irradiated to 15,000 Mwd per ton of uranium and punctured at 1 1/2-in. intervals was decanned in about 20 hr.⁵⁸ Rates were as much as 10 times greater than would be expected for unpunctured tubes. However, at one time the tube plugged at both ends, and it

was necessary to carry out a reduction operation to dislodge the plugs.

A process has been described for the recovery of fertile oxide materials from dispersion-clad fuel elements consisting predominantly of iron.⁵⁹ It consists in melting the iron, allowing the oxide to collect on the surface, and mechanically separating it from the molten metal.

Methods of processing uranium carbide fuels are being investigated on the gram scale at Atomics International. Two processes are being considered: (1) conversion of the carbide to uranium oxide in an oxygen atmosphere and subsequent reconversion to the carbide by reaction with carbon at elevated temperatures and (2) a process in which the carbide (or the oxide) is chlorinated, uranium chloride being volatilized to separate some fission products and then reconverted to uranium carbide. The oxidation of large quantities of uranium carbide presents problems in reaction rate control and in heat dissipation. A furnace has been constructed which utilizes a continuous screening apparatus for separation of the finely divided uranium oxide product.⁵⁷ On a 100-g scale the bulk of the reaction appears to be complete in about 45 min at about 400°C. However, it was found that a small amount (about 1 to 2 per cent) of the uranium carbide was not reacted, even after air oxidation at temperatures in the 500 to 550°C range for 1 to 2 hr. Fissia (fission oxide) resulting from the oxidation of uranium carbide has been chlorinated with a resultant volatilization of 84 per cent of the uranium as pure uranium tetrachloride.⁵⁷

In connection with the reconversion of oxide to carbide, it was found that ball-milling mixtures of UO_2 or U_3O_8 in carbon greatly increased the reaction rate on heating in vacuum.⁵⁷ Theoretical rate losses were obtained in $4\frac{1}{2}$ hr at 1350°C, with most of the carbon monoxide being evolved in 2 hr.

Studies are in progress at Oak Ridge on the release of gaseous fission products from irradiated uranium dioxide fuels. Although the objective of this work is to develop knowledge of the pressure buildup within the cladding of a fuel element on irradiation, the findings have some pertinence to fuel processing. Some of the factors involved have been discussed.⁶¹ A study of the release of iodine from high-density UO_2 during irradiation in the Oak Ridge reactor indicated that iodine release has the same temperature dependence as that of the release of

xenon and krypton, namely, diffusion controlled with high release at temperatures at which grain growth occurs.⁶² The chemical behavior of fission products in fissioning UO_2 is being studied. It is expected that rare earths will form oxides. No trouble from their introduction into the fuel is anticipated since they will not melt at anticipated reactor operating temperatures. Fission products, molybdenum, cesium, rubidium, technetium, ruthenium, rhodium, and palladium are likely to appear as metals. It is possible that these metals will form a liquid alloy which probably will be largely retained in the porous fuel matrix.

A program has been started at Battelle⁶³ to investigate fission-gas release from irradiated ceramic fuel materials during postirradiation heating. Apparatus developed for this study has been described.⁶³ Other fission-gas collection systems have also been described.^{42a, 64}

Liquid-Metal and Salt Processes

The possibilities of utilizing liquid-metal and salt systems for processing nuclear fuel materials are being explored at several atomic energy sites. The processes envisioned generally involve dissolution of the fuel material in a suitable liquid metal and subsequent purification steps which include selective crystallization, extraction by immiscible metals or molten salts, volatilization, and selective oxidations and reductions between metal and salt systems using electrolysis or appropriate salts and metals as oxidants and reductants. The product metal may be recovered by vaporizing the solvent metal. Solvent metals are therefore selected, not only on the basis of capability for dissolving appreciable amounts of metals of interest, such as uranium and plutonium, but also on the basis of having sufficiently high volatility to facilitate their eventual removal by volatilization. Metal solvents generally include zinc, cadmium, mercury, magnesium, and aluminum (although aluminum does have very low volatility).

To provide a firm background for process design, solubility data in the liquid-metal systems of interest are required for a great many elements—fissile, fission-product, and structural material elements. ANL has a fairly large program in this area for determining solubilities in zinc, cadmium, and magnesium. Solubilities have been reported for europium, gadolinium, dysprosium, erbium, manganese, alu-

minum, and nickel in cadmium over temperature ranges of interest.³⁷ The solid phases in equilibrium with the saturated solutions are also being determined.

Coprecipitation of various metallic elements is an important process phenomenon in process steps in which precipitation is employed to effect desirable separations. Coprecipitation may obstruct separations, but it can also be utilized to advantage. To gain a better understanding of coprecipitation in metal systems, a systematic study is under way³⁷ to ascertain the influence of atomic size, valence, and electronic configuration on coprecipitation of various elements from cadmium solution with cerium-cadmium intermetallic CeCd_{11} . The coprecipitation coefficient, λ , defined by the following equation:

$$\log \frac{\text{tracer in solution}}{\text{total tracer}} = \lambda \log \frac{\text{carrier in solution}}{\text{total carrier}}$$

has the values indicated for the following elements with CeCd_{11} : 0 for sodium, lithium, potassium, and yttrium; 0.099 for europium; 1.49 for lanthanum; 0.13 for uranium; 0.10 for strontium; and 0.04 for zirconium.

The existence of two intermetallic compounds in the uranium-zinc system has been conclu-

sively shown by vapor pressure studies, thermal analysis, X-ray and metallographic examinations, and chemical analysis.³⁷ Previously only one phase,^{65,66} originally identified as UZn_3 or as U_2Zn_{17} , had been thought to exist. The new phase, referred to as the epsilon phase, is richer in zinc and decomposes peritectically at about 840°C to form the U_2Zn_{17} , or delta phase. Chemical analyses of epsilon crystals indicate a uranium content of 23.7 to 24.6 per cent, compared to about 30 per cent for the delta phase.

Work was continued at ANL on the development of a liquid-metal process for recovery and suitable purification of fissionable material contained in crucible skull material remaining after melt-refining operations on EBR-II fission alloys. The processes under consideration presently utilize liquid zinc and magnesium systems as media in which recovery and purification operations are conducted. The present process, shown in Fig. IV-14, consists in freeing the skull material from the crucible by oxidation; selectively leaching the relatively noble fission products such as ruthenium and molybdenum with zinc; reducing the uranium oxides with magnesium dissolved in a separate zinc solution; and precipitating uranium in two successive steps for purification purposes, first as a uranium-zinc intermetallic from a zinc-rich solution and then as uranium metal from a magnesium-rich solution. A uranium metal

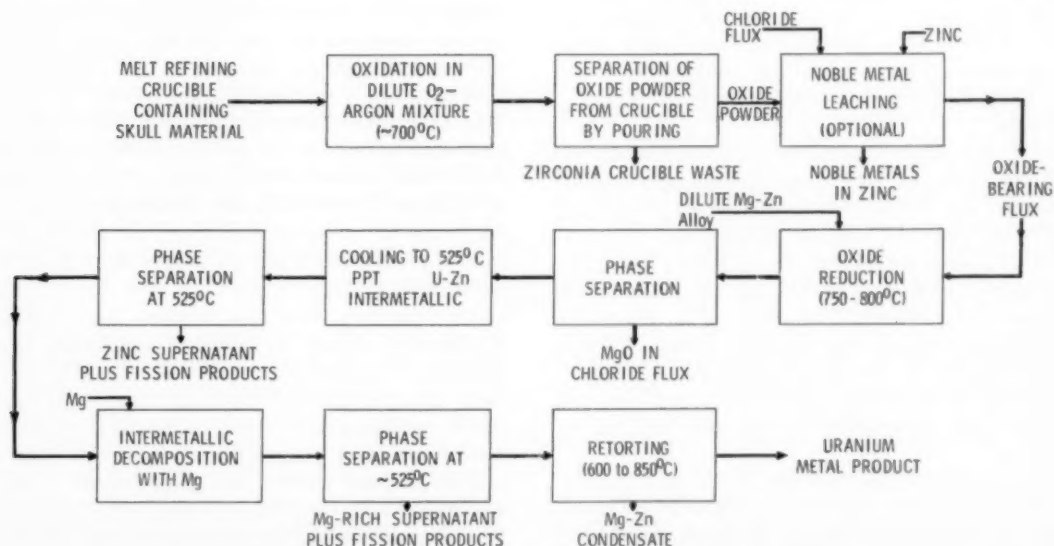


Fig. IV-14 Liquid-metal process for reclamation of melt-refining skulls.³⁷

product is then isolated by retorting to vaporize the associated solvent metals. This process differs from one shown in a previous Review⁶⁷ by incorporation of the noble metal leaching step and by reduction of uranium oxides in a dilute magnesium-zinc solution rather than in pure magnesium with a consequent reversal of the precipitation steps.

This process has been improved considerably through the use of one of several possible molten halide fluxes in conjunction with a magnesium-zinc reducing solution.³⁷ In the presence of a suitable flux and by adequate mixing, quantitative reductions of both pure uranium oxides and skull oxides were consistently obtained within 2 hr, and many were obtained within 30 min. Complete reduction of plutonium dioxide was similarly achieved. Another outstanding advantage of a flux is that it acts as a vehicle in which the magnesium oxide reaction product is suspended, thereby enabling a clean separation of this material from the metal phase. Physical removal of the magnesium oxide from a metal phase by filtration or through liquation of the magnesium oxide has been troublesome and unsatisfactory. A third advantage of the halide salt fluxes is that the reductions can, if desired, be conducted in an air atmosphere. Since unreduced uranium oxides are also suspended in the flux phase, a fourth potential benefit of a chloride flux arises from the possibility of reducing and leaching noble metals from the skull oxide with zinc prior to the reduction of uranium and the more stable fission-product oxides with magnesium. The removal of ruthenium from skull oxides by this procedure was demonstrated.

The salt fluxes found beneficial were mixtures of chlorides of alkali and alkaline-earth elements, the most rapid reductions occurring with the lighter cations. Magnesium chloride was a major ingredient in all fluxes that gave complete reduction within 30 min, and it is therefore presently regarded as an essential ingredient. Magnesium fluoride (5 mole %) was also present in all fluxes because of its effectiveness in providing clean and rapid coalescence and separation of the salt and metal phases.

A possible simplification of the process for isolation of plutonium bred in the uranium blanket of the EBR-II reactor involves the direct low-temperature (450°C) reaction of uranium with zinc in slight excess of stoichiometric to

give an intermetallic ($\text{UZn}_{14.5}$), which would then be treated with magnesium to decompose the intermetallic and dissolve the plutonium.³⁷ The low-temperature reaction was demonstrated with full-sized blanket pins 0.433 in. in diameter. Under the static conditions employed, reaction rates were slow (about 100 hr for complete reaction), but a substantial increase in reaction rates is thought to be possible.

A program is under way at ANL for evaluating materials to be used for containing liquid-metal systems of interest.³⁷ Graphite shows promise of being an outstanding container material. In a 100-hr holding run, a plutonium-zinc solution at 800°C was stable in a graphite crucible. The very slight attack of tantalum by zinc at 850°C is further reduced by the addition of magnesium. In preliminary tests a tantalum-7.5 per cent tungsten alloy has shown better resistance than tantalum to attack by zinc. A report⁶⁸ has been issued on studies of corrosion by molten zinc and cadmium systems.

A status report⁶⁹ has been issued on the Dow Chemical Company aluminum pyrometallurgical process on work done through fiscal year 1960. This process consists in dissolving uranium in molten aluminum, precipitating the uranium as UAl_3 by the addition of magnesium, separating the UAl_3 and dissociating it by treatment with zinc or magnesium, and retorting to vaporize the residual zinc or magnesium to enable recovery of a uranium metal product. Fission-product removals are effected by several mechanisms: volatility, insolubility in aluminum, and solubility in supernatant metal phases. This flow sheet and various modifications were evaluated in terms of application to an EBR-II fast-breeder-reactor fuel cycle. The behavior of uranium, plutonium, and fission products in the various process systems is discussed. Graphite was generally employed as the container material.

The process has two serious limitations: (1) limited ability to handle molybdenum and ruthenium without significant sacrifice of uranium and (2) difficulty in removing aluminum, which necessitates either extensive washing operations with magnesium or zinc with associated uranium losses or which, without washing, results in uranium products with residual aluminum contents of around 1 per cent. The effect of aluminum on radiation stability of the alloy has not been tested.

A second suggested application of the aluminum process is as a head-end step* in the processing of low uranium-zirconium fuel alloys. In molten aluminum, zirconium is converted by a process of exfoliation to an insoluble compound, $ZrAl_3$, and the uranium goes into solution in the aluminum. Nearly quantitative removal of zirconium may be effected, and uranium losses can be made small. Uranium may be subsequently precipitated from the aluminum solution as UAl_3 by the addition of magnesium, and, after separation, the UAl_3 may be dissolved in nitric acid to provide a feed solution to the Purex process.

Processes for thorium fuels are being studied at Atomics International. Thorium, present in a 25 per cent thorium-aluminum alloy, was largely separated from aluminum by dissolution of the alloy in zinc and precipitation of the thorium as the zincide.⁵⁶ The separation of uranium from thorium-uranium alloys by methods such as zone refining, electrorefining, and selective precipitation from liquid-metal solvents is also being investigated.^{56,58} Principal attention is being given to a process based on the high solubility of thorium in molten magnesium or magnesium-silver alloys and the contrasting low solubility of uranium. Small-scale active runs in which the uranium and thorium were separated, retorted, and arc melted into buttons showed approximately 5 per cent of the initial activity with the uranium and 15 per cent with the thorium.⁵⁸

A zinc solution and precipitation scheme was briefly examined for the processing of thorium-uranium fuels.⁷⁰ Although appreciable fission-product removal was realized in this preliminary work, low uranium and thorium recoveries suggest that a cautious interpretation of these removals should be made. Lead and thallium were found to be inefficient extractants of fission products from a uranium-thorium-aluminum alloy.⁷⁰

Thoria was reduced from molten cryolite by aluminum in graphite crucibles with nearly quantitative yields to make aluminum-20 wt.% thorium alloys directly.⁷¹ The reaction, when carried out at 1050°C, was complete in 30 min. Alloys up to 40 wt.% thorium may be produced. The reaction is presumably driven by the high free energy of formation of $ThAl_3$, estimated at

36.5 kcal. Some doubt existed previously as to the composition of the thorium-aluminum intermetallic compound. Runs specifically made for the purpose of identifying the thorium-aluminum compound resulted in the isolation of crystals that were unequivocally identified as $ThAl_3$.

This reduction process and the procedure for reducing uranium oxides in the skull reclamation process under investigation at ANL have features in common (such as the use of a flux and the suspension of the oxides in the flux). When thorium oxide is added to the molten fluoride salt, some of it dissolves in the salt, but most of it settles to the phase interface so that, in fact, an oxide slurry is present. It was postulated that the reaction proceeds most directly with the thoria which has settled near the interface and that the slower step which follows is that of depleting the dissolved thoria from the salt phase. A number of fluoride salt mixtures were investigated. It was concluded, however, that cryolite was the most promising reduction vehicle.

The reduction yield was markedly affected by the initial thorium content in the metal phase and dropped to near zero when the thorium concentration in the metal phase had increased to about 40 per cent. It was concluded that 40 wt.% thorium is at, or near, the practical limit of thorium buildup. Some indication was found that the salt phase could be reused, but, in general, the reduction of thorium appeared to decrease with the reuse of the salt phase.

A second report⁷² has been issued on the behavior of plutonium, uranium, and some fission products in a system where uranium-plutonium alloy is melted under calcium in a tantalum crucible. This work was previously reviewed⁷³ as Paper P/32 of the second Geneva Conference. Plutonium, uranium, and the noble fission products remain in the fuel alloy phase; the rare-earth and the alkaline-earth metals are extracted into the calcium. It was concluded that a process based on the use of molten calcium is feasible for the processing of metallic fuels from fast reactors, provided that either the melting point of the fuel is considerably less than 1000°C or that suitable materials of containment can be developed for use at higher temperatures. On the information presently available, the processing of metallic reactor fuels by molten calcium does not compare favorably with oxide slagging.

*U. S. Patent 2,963,361.

A discussion of electrorefining of plutonium is given in Sec. V, page 71 of this issue of *Reactor Fuel Processing*.

Crystallization of various metal phases from liquid-metal solutions is important in many of the liquid-metal processes under consideration. Benjamin and Strickland-Constable⁷⁴ have reported a study of solutions using solutions of zinc in mercury. A metastable region in which spontaneous nucleation could not occur extended to about 2°C below the saturation temperature. At temperatures below the metastable region, nucleation occurred at the walls and, perhaps, also on foreign particles. Stirring increased the rate of nucleation by a factor of about 5. The possibility that nucleation was occurring on foreign particles was somewhat ruled out by the fact that, when one crop of crystals was produced and then removed from the system by centrifugation, the rate of nucleation of other successive batches of crystals was not significantly reduced. The alternative explanations offered were: (1) that nucleation was occurring only at the walls and (2) that the presence of a small number of nuclei formed in the metastable region produced a crop of nuclei equal in number to that obtained by spontaneous nucleation at temperatures below the metastable region. In other words, the authors postulate that nuclei breed nuclei with a high reproduction factor.

The kinetics of reactions between liquid metals and salts is a continuing study of the Massachusetts Institute of Technology (MIT) Metallurgy Department. Various rate processes are discussed in a recent progress report.⁷⁵

Several patents have been issued which bear on liquid-metal and fused-salt processing:

1. Removal of rare-earth-metal fission products from liquid uranium-bismuth by extraction with fused halides.⁷⁶
2. Production of actinide metals by reducing their halides with appropriate reducing metals in the presence of a metal solvent such as zinc, cadmium, or mercury which is later distilled away.⁷⁷
3. Improvements relating to the electrolytic process for refining metals such as uranium, thorium, and niobium.⁷⁸
4. Reduction of yttrium fluoride to yttrium metal with calcium.⁷⁹
5. A process for recovery of nuclear fuels, specifically for separating uranium and plutonium by utilizing favorable distributions between

salt and metal phases.⁸⁰ Information on such a process was reported in an earlier Review.⁸¹

Miscellaneous. Apparatus and techniques were developed for the successful floating-zone refining of highly reactive metals.⁸² The technique consisted in employing a static inert atmosphere in hermetically sealed all-glass systems in which the atmospheric impurities are previously gettered on a discardable section of the bar that is being purified. This apparatus provides for an absolute minimum of contamination from gaseous impurities during the long melting procedures necessary for zone refining of highly reactive metals.

Methods have been described⁸³ for the production of pure metals such as hafnium, molybdenum, and zirconium by De Boer type processes (vaporization of halide and decomposition on hot wire). In connection with the production of ductile hafnium by means of vaporization and decomposition of the iodide, it was concluded that no substantial separation of zirconium from hafnium takes place. Ductile molybdenum was obtained by thermal dissociation of molybdenum pentachloride on a tungsten or molybdenum wire heated to 1300 or 1400°C. Separation of zirconium from zirconium carbide in a laboratory device in which iodine was reacted with the carbide to produce zirconium iodide was also described.

The vapor pressure of thorium was determined over the temperature interval of 1757 to 1956°K by the vacuum evaporation method of Langmuir.⁸⁴ The vapor pressure equation for Th(solid) to Th(gas) is as follows:

$$\log P_{\text{atm}} = \frac{-28,780}{T^{\circ}\text{K}} + 5.991$$

Derived thermodynamic data are presented.⁸⁴

Corrosion

Many of the chemical processing procedures under development involve unusually corrosive chemicals. As a result, various AEC contractors have, where necessary, established programs to determine what construction materials are most suitable for their processes and to define limitations beyond which these materials should not be used. It is not infrequently that developments in this area influence the develop-

ment of processes. In this section an effort is made to consolidate current information on such processes where programs have been established.

Solvent Extraction

The AEC is considering the processing of a large number of research- and power-reactor fuels. Many of these fuels cannot be processed in existing plants directly but must be subjected first to any one of several head-end procedures that produce aqueous solutions suitable for introduction into these plants. The development of these head-end procedures has presented some serious corrosion problems.

The Sulfex process is one of several head-end procedures developed for the purpose of removing the cladding from stainless-steel-clad fuels. Refluxing with 4M to 6M sulfuric acid is used in the process. Tests are being made to determine the limitations of low-carbon Nionel as a construction material in this system. The results^{1,85} of tests with 6M sulfuric acid, both with and without dissolved stainless-steel corrosion products, are shown in Table IV-11. The

Table IV-11 CORROSION OF LOW-CARBON NIONEL IN SULFEX DECLADDING SOLUTIONS^{1,85}

(Temperature: Refluxing; Reference Solution: 6M H₂SO₄; Exposure Times: 48 to 120 Hr)

Coupon location	Corrosion rate, mils/month, for the indicated conc. of S.S.-304 corrosion products	
	0 g/liter	10 g/liter
Liquid	3.3	0.7
Interface	2.6	1.4
Vapor	1.4	2.3

presence of dissolved stainless-steel corrosion products reduced the general attack by a factor of nearly 5. Specimens in the vapor phase, however, showed an increased attack. These results do not agree with those previously obtained at BMI under similar conditions. Some random pitting of interphase and liquid-phase specimens were observed in the solution containing corrosion product. Specimens from clean acid contained no pits.

In Sulfex decladding runs made in Hanford's recirculating-dissolver pilot-plant facility, substitution of steam for air during a gas sparging step decreased the corrosion rate of the dis-

solver vessel by 60 to 70 per cent. The vessel is fabricated from Hastelloy F alloy.⁸⁶ Further, the substitution of steam increased the rate of reaction with type 304L stainless-steel cladding.

The Hanford Hastelloy F pilot-plant dissolver is not only used for studies of the Sulfex process but also for the Niflex and Zirflex processes. Accumulated corrosion of the dissolver from these process studies has become increasingly apparent. A hole has appeared in the bulk metal of the dissolver behind a small bracket that had been installed in such a manner that a stagnant pocket had formed.⁸⁶ It is postulated that accelerated corrosion took place through a concentration cell mechanism. Visual inspection of internal surfaces has revealed (1) slight pitting of the heat-affected metal adjacent to welds and (2) general etching of nonheat-affected surfaces.

One method of processing uranium-molybdenum fuels [such as the Detroit Edison (Power Reactor Development Company) fuel] is to dissolve the fuel in a mixture of nitric acid-ferric nitrate. Container materials that have been considered suitable for use in this method include type 304 stainless steel, Hastelloy F, and Nionel. However, rates of attack of these materials by some nitric acid-ferric nitrate mixtures were as high as 12 to 13 mils/month.⁸⁷ In current studies, titanium 45A has been exposed to a solution simulating a final dissolver composition of 3M to 8M nitric acid, 0.5M ferric nitrate, and 0.02M molybdenum trioxide. In refluxing tests extending to 620 hr, the maximum observed corrosion was <0.1 mil/month.^{1,88} This is a considerable improvement over the other alloys tested.

The Savannah River Laboratory recently achieved the electrolytic dissolution of uranium-10 per cent molybdenum fuel. The electrolyte was 10M nitric acid. Tantalum and columbium are considered to be possible construction materials for the anode basket in a plant-sized electrolytic dissolver.⁸⁸ Both these metals are characterized by abnormally high overvoltage, thus making them inert during a normal electrolytic dissolution in which the impressed voltage does not exceed 10 volts. To determine whether high radiation fields alter the overvoltage characteristic, an electrolytic cell was set up in a radiation field of 10⁷ rep/hr. The cell was successfully operated up to an applied potential of 18 volts.⁸⁸

At the Savannah River Laboratory, the effect of the accumulation of stainless-steel corrosion products in nitric acid on the corrosion of a number of austenitic stainless steels is being studied. It is generally known that the accumulation of even traces of corrosion products in boiling concentrated nitric acid causes rapid intergranular degradation of the austenitic steels. The Savannah River Laboratory has explored the acid concentration range up to 4M, in which the effect of the presence of dissolved corrosion product is less known. The austenitic stainless steels tested included wrought 309SCb, 309SCb arc welded, 304L, and 304L heliarc welded with 308L. Several test solutions also included uranium. The results are shown in Fig. IV-15.

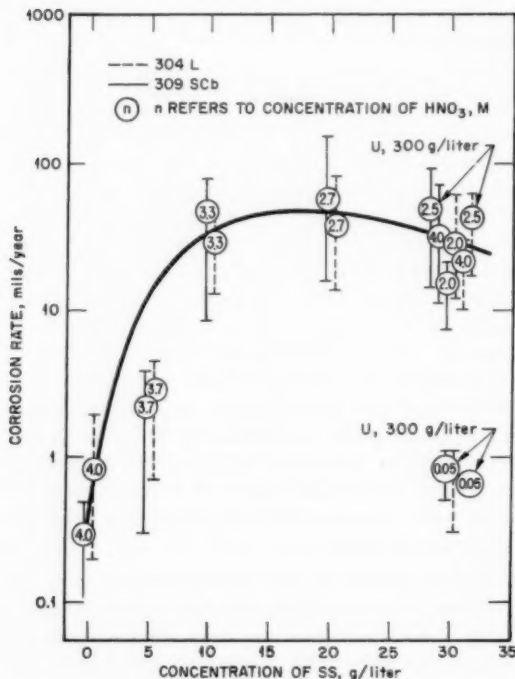


Fig. IV-15 Corrosion of types 304L and 309SCb stainless steels in boiling nitric acid that contained an accumulation of dissolved stainless-steel corrosion products.⁸⁸

Maximum corrosion rates of about 50 mils/year were observed with 15 to 20 g of dissolved stainless steel in the solution. Acid concentration up to 4M seemed to have little effect on the corrosion observed. Metallographic examination of the test coupons showed that intergranu-

lar attack occurred with wrought 304L, 308L welds, wrought 309SCb, and wrought 309SCb welds.⁸⁸

A report on the corrosion of stainless steel in nitric acid-hydrofluoric acid solutions has been published.⁸⁹ This work also originated at the Savannah River Laboratory. The incentive to do the work is associated with the possible processing of zirconium- or Zircaloy-clad fuels in the existing equipment at Savannah River. The bulk of the equipment is made from types 304L or 309SCb stainless steel. The acid concentration ranges employed were from zero to 10M nitric acid and 0.01M to 1.5M hydrofluoric acid. Temperatures ranged from 24°C to the boiling point. Weldments were included in the study, as was the effect of various additives such as zirconium, uranium, and aluminum. The generalized corrosion rates⁸⁹ of types 309SCb and 304L stainless steel as a function of acid concentration and temperature are shown in Figs. IV-16 and IV-17, respectively. The superiority of the stainless-steel type 309SCb alloy is evident. Also noteworthy is the reversal of the slope in the type 304L curve at room temperature. The corrosion rate decreases with increasing nitric acid content, whereas the inverse is true for the other three plots. The second of the four plots also shows that minimum corrosion occurs at a nitric acid concentration level of 1M. The Savannah River proposal for the dissolution of zirconium-clad fuels in nitric-hydrofluoric acid mixtures has subsequently been modified to 1M nitric acid-0.075M hydrofluoric acid from a previous 3M nitric acid-0.075M hydrofluoric acid. Considerably diminished localized weld-metal attack accompanied this change. Additions of zirconium tetrafluoride were found to increase the rate of attack because of the increased fluoride content. Additions of uranium as the nitrate decreased the corrosion rate of stainless-steel type 309SCb as long as the concentration of nitric acid was <3M. Additions of molybdenum similarly reduced the attack.

Hanford is planning to process and declad zirconium and stainless-steel fuels by the Zirflex process and the Sulfex process, respectively. Vacuum-melted Hastelloy F, although having some limitations, is the preferred construction material. As described in an earlier Review,¹⁷ Hanford, with the cooperation of Battelle, entered into an alloy-development program for the purpose of overcoming the sensi-

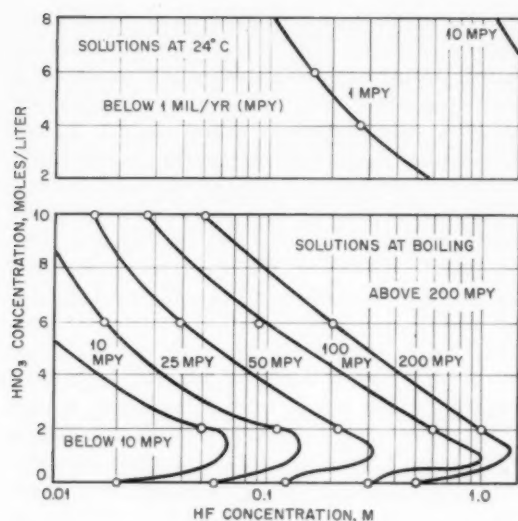


Fig. IV-16 Corrosion of type 309SCb stainless steel in nitric acid-hydrofluoric acid solutions.⁸⁹

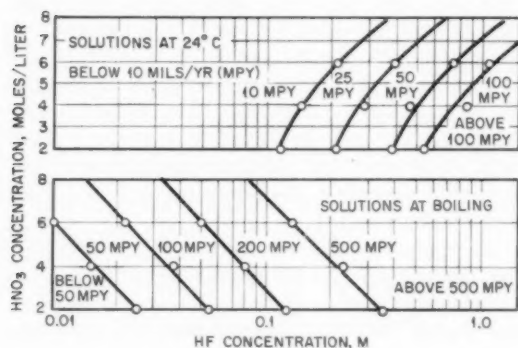


Fig. IV-17 Corrosion of type 304L stainless steel in nitric acid-hydrofluoric acid solutions.⁸⁹

tivity of Hastelloy F to intergranular penetration in areas adjacent to welds. The results of tests with the first set of 12 experimental nickel-chromium-base alloys was presented in the October 1960 issue of *Reactor Fuel Processing*. Battelle found that none of the alloys in the first set eliminated the attack when used as a filler metal for welding Hastelloy F. However, the alloys did appear to have some promise as a primary material of construction in nonwelded assemblies. Hence, the original concept of furnishing a satisfactory filler metal alloy has been abandoned, and a second set of 12 experimental alloys has been made for the purpose of im-

proving the alloys as base materials of construction. The synthesis and testing of the second set have now been completed, and BMI has issued a report covering the entire project.⁹⁰ The compositions of the second set of alloys are shown in Table IV-12. Welded specimens were subjected to aerated, boiling Sulfex solutions (3.5M sulfuric acid containing 20 g of dissolved stainless steel per liter) and boiling Niflex solutions (1M nitric acid-2M hydrofluoric acid). Alloys 23 and 24 were attacked at a rate of <0.3 mil/month in the Sulfex solution, whereas the

Table IV-12 COMPOSITIONS OF SECOND SET OF BMI EXPERIMENTAL ALLOYS⁹⁰

Alloy	Intended composition, * wt. %						
	Ni	Cr	Mo	Co	Fe	Ti	Cu
13	45	22	1.5		29.5	1	
14	45	22	4.5		26.5	1	
15	45	22	9		22	1	
16	45	22	9		21	1	1
17	50	25	1.5		21.5	1	
18	50	25	4.5		18.5	1	
19	50	25	6		17	1	
20	50	25	6		16	1	1
21	50	25	1.5		18.5	1	3
22	25	22	6	25	20	1	
23	25	25	6	25	17	1	
24	25	25	9	25	14	1	

*All alloys intended to contain 0.02 wt. % carbon, 0.6 wt. % manganese, and 0.4 wt. % silicon.

corresponding rates for other alloys ranged from 10 to 70 mils/month. However, alloys 23 and 24 were severely attacked in the Niflex solutions; weldments were penetrated at the end of five exposure periods of 25 hr each. In general, no selective attack in the heat-affected areas occurred except for slight indications in alloys 15, 16, 23, and 24. The only alloys that showed no preferential attack in the weld areas were alloys 18, 19, and 20. The experimenters concluded that, of the compositions studied, alloys 19 and 20 were optimum. Battelle suggests that further improvement might be obtained if the chromium and nickel contents were increased as far as possible without impairing workability.⁹⁰ Hanford^{53,54,86} has tested alloys 4, 11, 20, and 21. The effect of heat-treatment on corrosion rates in Niflex solutions and boiling 65 wt. % nitric acid was studied. Various annealing temperatures in the range of 1250 to 2150°F were included. No significant difference

in the corrosion rate was observed over the annealing temperature range or as the result of the method of quenching following annealing. Both rapid and slow cooling of samples following annealing were used.⁵³ Laboratory-scale dissolvers were fabricated from the four experimental BMI alloys for further testing.

A second report on the corrosion of alloys in aqueous hydrofluoric-nitric acid solutions was published at ICPP.⁹¹ Acid concentrations included in the study were 1M to 10M hydrofluoric acid and zero to 13M nitric acid. The following metals were tested: 309Cb, 316L, Carpenter-20 Cb, Hastelloy F, Incoloy 804, Monel, and tantalum. Exposure periods in all cases were 48 hr, and three periods were used for each test. Corrosion rates ranged from 140 to 936 mils/month. Since present allowable corrosion rates in the ICPP are considered to be 2 mils/month, the study was discontinued.

Hanford is exploring the possible applications of anodic passivation as a means of corrosion control in its process equipment. The first environment in which studies are being made is 67 wt.% sulfuric acid at 25°C, using stainless-steel type 304L as a construction material. In preliminary experiments, anodic passivation was achieved in 20 min at a current density of 3.4 ma/cm². Once established, passivation was maintained at a current density of 3 μ a/cm². No mention is made of the effect of this passivation on the corrosion rate.⁵³ In 65 wt.% nitric acid or in synthetic Purex 1WW waste solutions, no reductions in corrosion rates were achieved at any of the current densities tried.

Corrosion in Storing and Processing

Radioactive Wastes

In a recent report the results of a study of the corrosion of various materials in several neutralized radioactive wastes were reported.⁹² The study was made to determine the possibility of attaining greater economy in the storage of wastes by using either large carbon steel or less expensive stainless-steel tanks. The three types of wastes considered were as follows:

(1) caustic-neutralized hydrofluoric acid containing wastes from the processing of zirconium fuels (STR process), (2) caustic-neutralized aluminum nitrate wastes (Redox process), and (3) aluminum nitrate wastes treated with paraformaldehyde. Fifty per cent caustic was added to the first two wastes until pH 10 was achieved.

The materials tested included welded mild steel, and types 304L and 347Cb stainless steel. A fourth material (ASTM A285-54T grade C, a low-alloy steel) was tested in the third waste solution only. Exposure times were 3, 6, and 12 months, and the test temperature was 60°C. In the neutralized zirconium process waste, mild steel showed general rates of attack which would normally be considered acceptable: <0.1 mil/month. However, the specimens suffered a pitting type of attack in all three phases (liquid, interface, and vapor) for all testing periods, and, hence, mild steel cannot be recommended as a construction material for storage tanks. Both stainless steels were satisfactory in both their resistance to general corrosion and in resistance to pitting. In the second solution, localized pitting was evident on mild-steel specimens at both the interface and in the vapor phase. No pitting was observed in the liquid phase. In the aluminum nitrate waste treated with paraformaldehyde, the surface corrosion rate of carbon steel was sufficiently high to effect the corrosion of the identifying numbers of the specimens beyond recognition after 12 hr. In this case also, the two austenitic stainless steels (types 304L and 347Cb) performed satisfactorily. It was concluded in the report that mild steel could not be recommended as a construction material for storage of any of the three wastes tested.

Corrosion testing has been continued at ORNL for the purpose of evaluating the resistance of materials for storage of wastes resulting from the Purex 1WW process, in which the feed was the product from Darex dissolutions.⁹⁵ Since the composition of the Purex 1WW stream undergoes some variation from time to time, a synthetic composition that is considered to be reasonably typical of the stream has been selected. Tests were made with both 2M and 5M nitric acid containing 100 ppm chloride ion and 1.82M stainless-steel dissolution product. The corrosion observed is predominantly intergranular in nature, and the results in Table IV-13 are the values obtained by metallographic observation. It is not yet known whether this amount of corrosion is acceptable for long-term storage. Longer test exposures are needed to resolve this problem.

Five of the experimental nickel-chromium-base alloys prepared by BMI were also evaluated for use in boiling Purex 1WW waste solutions.⁵³ All specimens were evaluated as weldments,

Table IV-13 CORROSION OF STAINLESS STEELS IN SYNTHETIC DAREX-PUREX 1WW WASTE⁸⁵

(Composition: Acid as Shown, 100 Ppm; 1.82M Dissolved Stainless Steel; Duration of Tests: 1000 to 2500 Hr)

	Temp., °C	Intergranular attack, mils	
		2M HNO ₃	5M HNO ₃
S.S.-304L	50	0.5	0.5
	65	1	
	80	1-3	1
S.S.-347	50	0.5	0.5
	80	1	1.5-2

both self-welded and welded with type 304L stainless steel. Corrosion of the base metal was somewhat less than that for stainless-steel type 304L. Two of the self-welded BMI samples were attacked preferentially in the weld metal. This attack may have occurred as a result of effects brought about by a loss of inert sparge gas during welding. It has been observed that the corrosiveness of the Purex 1WW stream to both stainless-steel type 304L and the experimental nickel-base alloys can be reduced markedly (perhaps by as much as a factor of 10) by the conversion of the hexavalent chromium present in the waste to the trivalent chromium. One way of obtaining this reduction is to reflux the Purex 1WW with 0.05M ferrous ammonium nitrate and 0.1M sulfamic acid.⁵³

Fluoride-Volatility Processing Methods

ORNL is exploring the possibility of converting UF₄ to UF₆ by the Fluorox process. In this process, uranium is oxidized to the hexavalent state with dry air or oxygen in a continuous 4-in.-diameter fluidized-bed reactor, in which bed temperatures of 700 to 850°C are normally used. Corrosion evaluations are being made coincident with process studies.⁹³ By utilizing a variety of techniques of corrosion evaluation, it has been established that the attack on the Inconel vessel walls in the fluid-bed region has been on the order of 150 to 700 mils/year when the bed was maintained at an operating temperature of 860°C. It is expected that wall temperatures are 50 to 150°C higher. A 10- to 20-mil-thick scale (composed of metal fluorides, metal oxide corrosion products, and various uranium compounds from the bed) formed on the reactor wall. It is thought that this scale prevented the rate of attack from in-

creasing to as much as inches per year. Dimensional change was one of the criteria used for corrosion evaluation. A second criterion was the increase of metallic fluoride content (other than uranium) of the product. Exposed metal was also examined metallographically, but it is not clear from the report whether the measurements made in this manner reflected dimensional changes or intergranular attack. Some evidence suggests that, if thermal cycles were eliminated, the corrosion rates would be about 100 to 300 mils/year. In general, corrosion was fairly uniform, except for a narrow zone in the middle of the reactor where some pitting was observed. The authors recognize that, if Inconel is to be used as a construction material for a production reactor, some provision would have to be made for replacing the fluid-bed section on a routine basis.⁹³

One of the methods proposed for processing zirconium-matrix fuels is the Zircex process, consisting of three steps. The fuel is first hydrochlorinated at temperatures of 300 to 600°C. The bulk of the zirconium is removed from the system as volatile zirconium tetrachloride. The residue, which contains uranium, is chlorinated with carbon tetrachloride vapors, thus converting the uranium to the volatile tetrachloride, which is condensed in a second vessel. The uranium can either be dissolved in nitric acid or converted to UF₆ by contacting with fluorine. In scouting corrosion tests, in which 15 materials were exposed to hydrogen chloride and nitrogen-diluted carbon tetrachloride vapors, it was determined that the carbon tetrachloride part of the cycle was the most corrosive. Corrosion rates at 600°C were found to be 10 times greater than the rate at 400°C.^{84,95} Current results are shown in Table IV-14.

In the ARCO process under development at ICPP, zirconium-uranium fuels are dissolved in a mixture of lead-lead chloride at 520°C. The zirconium dissolution product is removed as the volatile tetrachloride, leaving behind the product salt containing uranium (principally as the trichloride), together with excess lead chloride and the alkali, alkaline-earth, and rare-earth fission products. Uranium salts are quantitatively leached from the lead chloride product matrix with 8M nitric acid. Following feed adjustment, this is introduced into the solvent-extraction plant. The report on the process, including corrosion evaluations, has been published.⁹⁶ Preliminary information reported in

Table IV-14 CORROSION OF PROPOSED MATERIALS TO ZIRCEX PROCESS ENVIRONMENTS^{84,85} AT 600°C

Alloy	Observed corrosion, mils/month
<i>1-Hr Exposure⁸⁵ to CCl₄</i>	
Nichrome-V	5.5
Inconel	18
Chlorimet-2	32
Pyroceram 9608	1.0
<i>13-Hr Zircex Cycle⁸⁴</i>	
S-816	29
Chlorimet-2	12
Hastelloy B	46
S.S.-316	20
S.S.-329	213

*Zircex cycle: (1) HCl, 11 hr, 600°C; (2) CCl₄ vapor plus N₂, 1 hr, 600°C; (3) O₂, 5 min, 600°C; and (4) N₂ plus CCl₄ vapor, 1 hr, 600°C.

the preceding Review has been expanded in the present report to include alloys other than nickel alloys. In addition, the report presents the results of metallographic examinations of all the alloys studied (including the nickel alloys). In tests with molybdenum in the lead-lead chloride system at 520°C, the average weight loss corresponded to a rate of attack of 4 mils/month; however, interfacial effects at the junction of the lead and lead chloride phases were severe. Niobium showed no particular advantage over any of the nickel alloys tested. Metallographic examinations have shown no grain boundary or intergranular attack on Hastelloy F, Incoloy 804, or Carpenter-20. Some grain-boundary attack was observed at depths of 10 mils in Inconel X.⁹⁶

A fused-salt process is under development at HAPO for the recovery of the uranium values from U₃O₈. The process consists in chlorinating U₃O₈ with chlorine or hydrogen chloride in an equimolar melt of sodium chloride-potassium chloride. The temperatures used are 750 to 800°C. In a second step, uranium dioxide is deposited at the cathode by electrolysis of the molten-salt solution. In corrosion tests being made on the first step of this system at BMI, the melt is sparged with a mixture of chlorine, oxygen, and argon gases for 4 hr, then with chlorine and argon for 4 hr for a total exposure time of 8 hr.^{97,98} Specimens are exposed at three locations: (1) in the melt below the sparge tube, (2) in the melt adjacent to the sparge tube, and (3) at the vapor-liquid interface of the melt

above the sparge tube. Metals considered included cobalt-, iron-, nickel-, niobium-, and tantalum-base alloys, together with pure metals such as silicon and tantalum. None of the materials investigated, except silicon, has shown rates of attack of less than several hundred mils per month in all three specimen locations. The corrosion rate of silicon has not exceeded about 10 mils/month.

Testing of a large number of materials in the hydrochlorinated chloride melt (equimolar sodium chloride-potassium chloride) is being made at Hanford. Test temperatures are similar to those used at Battelle. Nickel alloys and the 300- and 400-series stainless steels all corroded at rates in excess of 200 or more mils per month.⁵³⁻⁵⁵ Aluminum-containing alloys, such as Alnico-2, -3, and -3B, have shown the greatest promise with rates not exceeding 50 mils/month;⁵⁵ however, some accelerated attack at the interface and in the vapor phase has been observed. Several tests have been made in a lower melting system: lead chloride-potassium chloride at 500°C. Samples of nickel-base alloys (Hastelloy B, D, and W) exposed to this less severe environment corroded at rates of 100, 18, and 81 mils/month, respectively.⁵⁴

Corrosion testing is continuing at BNL on a process in which fuels are dissolved in nitrogen dioxide-hydrogen fluoride mixtures. The effect of the presence of water vapor in 30 mole % nitrogen dioxide-70 mole % hydrogen fluoride solution has been determined. At 100°C the rate of attack increased from 0.15 to 0.56 mil/month.⁹⁹ As has been noted in earlier Reviews, zirconium dissolution and drying of the resulting zirconium salts intensify the corrosion of Monel. Under these circumstances, nickel has been found to be superior to either Monel or Inconel. New materials which show promise include Nionel, gold, platinum, INOR-8, and Genetron plastic VK-240.

Pyrometallurgical Processing

Pyrometallurgical processes for the recovery of nuclear reactor fuel include most of the non-aqueous methods that operate at elevated temperatures, the fluoride-volatility processes being notable exceptions. Methods developed at ANL for the processing of EBR-II fuel include oxidative slagging in an oxide crucible at temperatures well above the uranium melting point.

Table IV-15 CORROSION IN MOLTEN CADMIUM SYSTEMS¹⁰⁰

Molten metal*	Test material	Temp., °C	Corrosion observed
<i>100-Hr Static Tests</i>			
Cd	S.S.-410, mild steel	550	No wetting; no attack
	tantalum		
2 U-Cd	S.S.-410, mild steel	550	No attack
Cd	S.S.-304 and 310	550	Intergranular attack
2-8 Zn-0.2 Mg-Cd†	S.S.-410, mild steel	550	No attack
10 Zn-0.2 Mg-Cd	S.S.-410, mild steel	550	Slight intergranular attack
2-50 Mg-Cd‡	S.S.-410, mild steel	650	Surfaces wetted; no attack
Cd	S.S.-410, mild steel	700	Intergranular attack
10 Zn-0.2 Mg-Cd	S.S.-410, mild steel	700	Intergranular attack
<i>1000-Hr Rotating Capsule Tests</i>			
Cd	Mild steel	550	No attack
2 U-Cd	Mild steel	550	No attack
5 Mg-Cd	Mild steel	550	No attack
2-8 Zn-0.2 Mg-Cd†	S.S.-410, mild steel	350	No attack
10 Zn-0.2 Mg-Cd	S.S.-410, mild steel	350	Slight attack
<i>Thermal-Convection Loop Tests</i>			
30 Mg-Cd	Medium carbon steel	575-675 (144 hr)	Mass transfer deposit, 2.5 mils; hot leg pitted
15 Mg-Cd	Medium carbon steel	630-725 (1004 hr)	Mass transfer deposit, 6 mils
<i>Forced-Convection Loop Tests</i>			
2 U-0.2 Mg-Cd	Medium carbon steel	550 (1000 hr)	No major corrosion
0.85 U-2 Mg-Cd	Medium carbon steel	550 (4800 hr)	No corrosion observed

*Concentrations are expressed as weight per cent.

†Concentrations of zinc varied between 2 and 8 wt. %.

‡Concentrations of magnesium varied between 2 and 50 wt. %.

Table IV-16 CORROSION IN MOLTEN ZINC ENVIRONMENTS¹⁰⁰ AT 750°C

(100-Hr Static Tests)

Molten metal*	Test material	Corrosion observed
Zn	Tungsten	No corrosion
Zn	Tantalum	Mild corrosion through formation of inter-metallic
Zn	Molybdenum	Mild corrosion through dissolution
5-46 Mg-Zn†	Tantalum	No corrosion
5-46 Mg-Zn†	Molybdenum	Mild corrosion through dissolution
Zn	Titanium	Severe corrosion
46 Mg-Zn	Cobalt alloys	Severe corrosion
46 Mg-Zn	Tungsten alloys	Severe corrosion

*Concentrations are expressed as weight per cent.

†Concentration of magnesium was varied between 5 and 46 wt. %.

Other techniques include dissolution and crystallization in liquid-metal media. Construction materials for these processes are required to withstand a variety of molten-metal environments with an acceptable amount of corrosion.

A report on the study of corrosion characteristics of molten zinc and cadmium solvents has been published.⁶⁸ Various testing techniques were used, including 100-hr static tests, 1000-hr rotating-capsule tests, thermal-convection loops, and forced-convection loops. All four testing techniques were utilized in studying molten cadmium systems, whereas the 100-hr static tests were used exclusively for the zinc environments. The results of these tests are shown in Tables IV-15 and IV-16. In general, stainless-steel type 410, mild steel, and tantalum resisted most of the cadmium melts tested at temperatures of 550°C. Melt

additions of a few per cent uranium, 2 to 50 per cent magnesium, or 2 to 8 per cent zinc did not alter the corrosion characteristics to any great extent. When cadmium temperatures were raised to 700°C, intergranular attack of stainless-steel type 410 and mild steel occurred. The 300-series stainless steels were attacked severely at grain boundaries, apparently by a leaching mechanism of the constituent nickel. The results of the 1000-hr rotating-capsule tests were similar to those obtained in 100-hr static tests. Slight attack was observed in 10 per cent zinc-cadmium solutions at 350°C.

Two thermal-convection loop tests were made with magnesium-cadmium systems at temperatures ranging from 575 to 725°C. Test times on the two loops were 144 and 1004 hr, respectively. Mass-transfer deposits of iron occurred in the first loop to the extent of 2.5 mils, and similar deposits of 6 mils were observed in the second loop. In two forced-convection loop tests, no major corrosion of medium carbon steel was observed in cadmium containing up to 2 per cent uranium and magnesium.

Molten zinc systems have been known to be very corrosive to metals. In 100-hr static tests at 750°C, nitrided and cyanided steels, cobalt alloys, titanium, and tungsten alloys either completely disintegrated or were severely corroded. Tungsten was the only metal that remained inert. Although tantalum showed some resistance to attack by molten zinc, it interacted with pure zinc to form an intermetallic phase. The thickness of the interaction varied somewhat from specimen to specimen but was generally 1 mil or slightly greater. Additions of magnesium to the zinc to the extent of 5 to 46 wt.% reduced the corrosion of tantalum to the point where none was observed. Molybdenum was the only other metal which remained intact after exposure to molten zinc. Metallographic examination indicated that slight corrosion had occurred. This observation was confirmed by the presence of molybdenum in the zinc phase to an extent of its solubility, 0.02 wt.%.

Several ceramic materials were tested by themselves and as refractory coatings on mild steel in both molten zinc and molten 46 wt.% magnesium-zinc. With the exception of silicon nitride and Vycor, the ceramics were inert to both environments. However, when the ceramics were used as coatings to protect mild steel, they proved to be easily penetrated by molten zinc

and, in all cases but one, by the magnesium-zinc alloy.

Corrosion testing of tantalum in molten plutonium for application in the LAMPRE-I reactor is continuing.¹⁰⁰ It has been demonstrated that arc-melted tantalum possesses superior corrosion resistance, in both the annealed and the as-worked conditions, to that of ordinary tantalum. Differences in the metallographic structure are also apparent in that the arc-melted tantalum appears cleaner. The beneficial effects of carbon addition have been confirmed, but there is now evidence that the temperature of exposure must be high enough to convert graphite to plutonium carbide in order to provide protection to the capsule, unless the carbide is added instead of graphite. The presence of calcium or magnesium in the fuel has been shown to affect the corrosion resistance of tantalum adversely, even in the presence of carbon. Both aluminum and, in particular, silicon have proved to be beneficial in this respect. Further tests are under way to verify these indications. Tests are now in progress on a high-purity tantalum alloy with 0.1 wt.% tungsten. The tungsten is added because of its nearly complete immunity to the cast iron-plutonium fuel alloy.

Homogeneous Reactor Fuel Processing

The reactor concept in which fissionable material is dispersed or dissolved homogeneously in a fluid has several advantages to recommend it. One of these is that a side stream of the fuel can be removed either continuously or on a batch basis for the purpose of processing for removal of fission-product poisons. The aqueous Homogeneous Reactor Test (HRT) at Oak Ridge is one such reactor, and a chemical processing plant has been constructed as an integral part of the installation.

Micron-sized solids continuously form during the course of operation of the HRT. These solids are either insoluble activated corrosion products or fission products. The original processing plant provided several hydroclones to effect separation of this solid constituent. Since the efficiency of the original installation was lower than expected, one of the hydroclones was replaced by a multiple hydroclone unit containing 13 0.6-in. hydroclones in parallel, which in turn

fed the original second hydroclone in series. This installation, which was operated for a total of 4500 hr, was also removed. Pressure-drop and mixing-rate tests performed after removal indicated that one to three hydroclone feed ports were partially plugged. An accumulation of solids at these locations was also indicated by radiation survey. The replacement multiple hydroclone will consist of 18 0.4-in. hydroclones in parallel. Rather extensive tests are being performed on both the new and the old multiple hydroclones.

An experimental device for measuring the quantity of solids accumulated in the replacement hydroclone underflow pot was built and will be tested in the next run. The principle of the detector is based on the difference in specific gamma activity of solids that have accumulated in the underflow receiver and the reactor fuel. With the reactor operating at 5 Mw and the multicclone collecting solids at a rate of 1 to 2 g/hr, the gamma field at the center of a settled bed of 500 g of solids has been estimated to be 2×10^6 r/hr. The gamma field at the center of the pot due to fuel solution only will be 20 to 30 per cent of this value. Gamma heating, and therefore temperature, will be a function of the gamma flux, thus making it possible to estimate the depth of the settled bed of solids.¹⁰¹

The multiple hydroclone assembly is designed to remove only solid particles from the fuel. Occasionally the entire fuel batch must be processed to remove the accumulated soluble contaminants, principally corrosion-product nickel. Studies being made in the laboratory for specific removal of corrosion-product nickel have been reported previously. In the past the soluble poisons have been extracted from the reactor fuel by processing the entire fuel batch by solvent extraction. Other alternates are being examined. One such alternate is a process based on (1) precipitation of uranyl peroxide; (2) separation of the filtrate containing the contaminants; and (3) regeneration of the fuel by destroying the peroxide, followed by addition of acid and copper in the required amounts. It is felt that the equipment for this process could be installed in existing cells and operated in a heavy-water system. The following process requirements apply:

1. Uranium recovery to be in excess of 90 per cent.
2. Decontamination factor for soluble impurities to be >10.

3. A filtration rate capacity to exceed 20 liters/(hr)(sq ft).

Present studies are being made with a synthetic solution having a uranium concentration of 150 g/liter. Scouting tests have shown that there is no particular advantage in the use of more dilute solutions, and the entire 8-kg reactor charge may be processed in one batch in a 6-in.-diameter critically safe vessel at the original uranium concentration.

A study of the adsorption characteristics of xenon and krypton on AGOT-grade graphite has been completed and a report published.¹⁰² Adsorption isotherms of xenon-helium mixtures were determined at -79, 0, 20, 30, and 80°C, in order to determine whether the presence of helium affects the adsorption behavior of xenon. The isotherms obtained from xenon-helium mixtures were essentially the same as those obtained using pure xenon gas. The temperature dependence of the adsorption behavior shows a heat of adsorption for xenon of about 3500 cal/

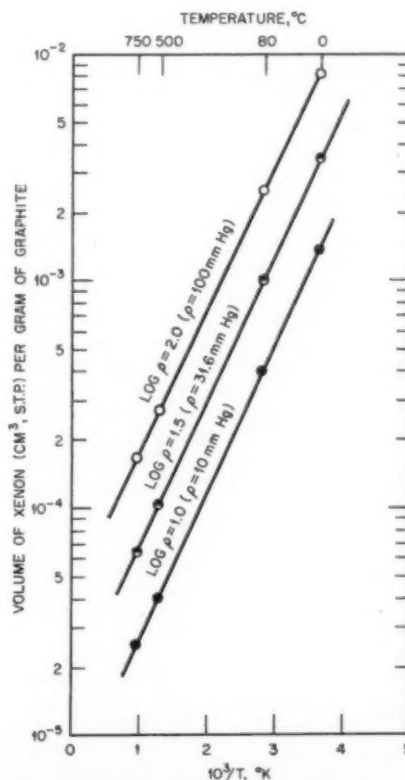


Fig. IV-18 Xenon adsorption on AGOT graphite.¹⁰²

mole, which is close to the published heat of condensation. This is an indication that the adsorption is physical. Typical adsorption isobars¹⁰² obtained together with extrapolations up to 750°C are shown in Fig. IV-18.

References

1. R. E. Blanco, Chemical Technology Division, Chemical Development Section B, Monthly Progress Report for September 1960, USAEC Report CF-60-10-91, Oak Ridge National Laboratory, Jan. 19, 1961.
2. R. E. Blanco, Chemical Technology Division, Chemical Development Section B, Monthly Progress Report for June-July 1960, USAEC Report CF-60-7-76, Oak Ridge National Laboratory, Dec. 12, 1960.
3. R. E. Blanco, Chemical Technology Division, Chemical Development Section B, Monthly Progress Report for May 1960, USAEC Report CF-60-6-108, Oak Ridge National Laboratory, Nov. 11, 1960.
4. F. L. Culler, Jr., Chemical Technology Division Monthly Report for October 1960, USAEC Report CF-60-10-118, Oak Ridge National Laboratory, Oct. 31, 1960.
5. National Lead Co. of Ohio, Summary Technical Report for the Period July 1, 1960, to September 30, 1960, USAEC Report NLCO-820, Oct. 28, 1960.
6. W. D. Arnold and D. J. Crouse, Further Evaluation of Amines as Extractants for Uranium from Sulfate Liquors, USAEC Report ORNL-3030, Oak Ridge National Laboratory, Jan. 12, 1961.
7. M. de Trentinian and A. Chesne, Extraction and Purification of Plutonium by a Tertiary Amine, French Report CEA-1426, 1960.
8. M. Zifferero and F. Baroncelli, Behavior of Some Tertiary Aliphatic Amines in the Extraction of Uranium Aqueous Solutions and Fission Products, Italian Report CNC-41, July 1960.
9. F. L. Culler, Jr., Chemical Technology Division Monthly Report for November 1960, USAEC Report CF-60-11-118, Oak Ridge National Laboratory.
10. F. J. Hurst and D. J. Crouse, Recovery of Uranium from Di-2-ethylhexyl Phosphoric Acid (Dapex) Extractant with Ammonium Carbonate, USAEC Report ORNL-2952, Oak Ridge National Laboratory, July 14, 1960.
11. K. B. Brown, Chemical Technology Division, Chemical Development Section C, Monthly Progress Report for June-July 1960, USAEC Report CF-60-7-108, Oak Ridge National Laboratory, Sept. 26, 1960.
12. K. B. Brown, Chemical Technology Division, Chemical Development Section C, Monthly Progress Report for August-September 1960, USAEC Report CF-60-9-119, Oak Ridge National Laboratory, Dec. 29, 1960.
13. R. D. Baybarz and R. E. Leuze, Separation of Transplutonium and Rare Earth Elements by Liquid-Liquid Extraction, USAEC Report CF-60-3-22, Oak Ridge National Laboratory, June 6, 1960.
14. L. E. Marc de Chazal and A. R. Lister, The Use of Diamylamyl Phosphonate (DAAP) as an Alternative Extractant to TBP, British Report AERE-M-698, May 1960.
15. K. B. Brown, Chemical Technology Division, Chemical Development Section C, Monthly Progress Report for April-May 1960, USAEC Report CF-60-5-114, Oak Ridge National Laboratory, July 12, 1960.
16. R. M. Wagner and R. S. Farrand, Radiation Stability of Organic Liquids, Semiannual Report No. 6 for July 1, 1959, to December 1, 1959, USAEC Report TID-5635, Stanford Research Institute, Dec. 31, 1959.
17. *Reactor Fuel Processing*, 3(4): 19 (October 1960).
18. L. H. Towle and R. S. Farrand, Radiation Stability of Organic Liquids, Semiannual Report No. 7 for January 1, 1960, to June 30, 1960, USAEC Report TID-6186, Stanford Research Institute, June 15, 1960.
19. F. L. Culler, Jr., Chemical Technology Division Monthly Report for September 1960, USAEC Report CF-60-9-113, Oak Ridge National Laboratory, Sept. 30, 1960.
20. J. W. Simmons, ed., Summary Technical Report for the Period October 1, 1959, to December 31, 1959, USAEC Report NLCO-800, National Lead Co. of Ohio, Jan. 22, 1960.
21. V. B. Shevchenko and V. S. Smelov, Problem of the Mechanism of Plutonium Nitrate Extraction by Mono- and Dibutyl Phosphates, USAEC Translation AEC-tr-3957, 1959.
22. J. J. Shefcik, Dares Pilot Plant Studies, USAEC Report HW-62537, Hanford Atomic Products Operation, Oct. 29, 1959.
23. R. W. McKee, Trough-Tray Dissolver, USAEC Report HW-60823, Hanford Atomic Products Operation, June 26, 1959.
24. P. W. Smith, The Pilot Plant Operation of a Vertical Tube, Recirculating Dissolver for the Dissolution of Uranium Dioxide in Nitric Acid, USAEC Report HW-64416, Hanford Atomic Products Operation, Mar. 21, 1960.
25. J. Dunn and R. J. Sloat, Development and Testing of an Improved Agitator for the Redox and Purex Separations Plants, USAEC Report HW-63175, Hanford Atomic Products Operation, Dec. 24, 1959.
26. P. S. Kingsley and M. L. Short, Decontamination, USAEC Report HW-63110, Hanford Atomic Products Operation, June 1, 1960.
27. W. T. McDuffee, Power Reactor Fuel Process-

- ing Pilot Plant, Brookhaven Fuel Program, USAEC Report ORNL-3013, Oak Ridge National Laboratory, Dec. 15, 1960.
28. J. M. Atwood and W. A. Snyder, eds., Plutonium Recycle Program Annual Report for Fiscal Year 1959, USAEC Report HW-62000, Hanford Atomic Products Operation, Oct. 15, 1959.
 29. *Reactor Fuel Processing*, 2(2): 16 (April 1959).
 30. R. W. Durham and A. M. Aikin, Concentration and Purification of Plutonium Solutions by Ion Exchange Columns, Canadian Report CEI-55, Feb. 12, 1953.
 31. F. L. Culler, Jr., Chemical Technology Division Monthly Report for December 1960, USAEC Report CF-60-12-94, Oak Ridge National Laboratory, Dec. 31, 1960.
 32. T. F. Demmitt, High Flow Rate Operation of a Duplex Ion Exchange System, USAEC Report HW-65478, Hanford Atomic Products Operation, June 2, 1960.
 33. Oak Ridge National Laboratory, Chemistry Division Annual Progress Report for Period Ending June 20, 1960, USAEC Report ORNL-2983, Sept. 22, 1960.
 34. K. A. Kraus et al., Ion-Exchange Properties of Hydrous Oxides, in *Progress in Nuclear Energy, Series IV, Technology*, Vol. 2, pp. 73-91, Pergamon Press, New York, 1960.
 35. S. Lawroski et al., Chemical Engineering Division Summary Report for July, August, and September 1960, USAEC Report ANL-6231, Argonne National Laboratory, February 1961.
 36. F. W. Miles and W. H. Carr, Engineering Evaluation of Volatility Pilot Plant Equipment, USAEC Report CF-60-7-65, Oak Ridge National Laboratory, Sept. 30, 1960.
 37. S. Lawroski, Argonne National Laboratory, March 1961. (Unpublished)
 38. T. R. Johnson et al., Nitridation of Crucible Skulls from Melt Refining, USAEC Report ANL-6211, Argonne National Laboratory, September 1960.
 39. J. E. A. Graae et al., A Radiation Stable Heavy Duty Electromechanical Manipulator, in Proceedings of the Eighth Conference on Hot Laboratories and Equipment, San Francisco, California, December 13-15, 1960, USAEC Report TID-7599 (Bk. 1), pp. 239-251.
 40. V. G. Trice, Jr., and N. R. Chellew, *Nuclear Sci. and Eng.*, 9(1): 55-58 (January 1961).
 41. A. Schneider and N. R. Chellew, *Nuclear Sci. and Eng.*, 9(1): 59-63 (January 1961).
 42. *Reactor Fuel Processing*, 4(1): 31-32 (January 1961).
 - 42a. R. E. Womack, A Fission Gas Collection System, in Proceedings of the Eighth Conference on Hot Laboratories and Equipment, San Francisco, California, December 13-15, 1960, USAEC Report TID-7599 (Bk. 2), pp. 441-449.
 43. N. R. Chellew et al., *Nuclear Sci. and Eng.*, 9(1): 64-70 (January 1961).
 44. J. Wolkoff and A. A. Chilenskas, *Nuclear Sci. and Eng.*, 9(1): 71-77 (January 1961).
 45. N. R. Chellew and V. G. Trice, Jr., *Nuclear Sci. and Eng.*, 9(1): 78-81 (January 1961).
 46. N. R. Chellew and M. Ader, *Nuclear Sci. and Eng.*, 9(1): 82-86 (January 1961).
 47. N. R. Chellew and G. A. Bennett, *Nuclear Sci. and Eng.*, 9(1): 87-90 (January 1961).
 48. L. J. Mullins et al., Removal of Fission-Product Elements from Plutonium by Liquefaction, in *Extractive and Physical Metallurgy of Plutonium and Its Alloys*, pp. 101-108, Interscience Publishers, Inc., New York, 1960.
 49. W. D. Wilkinson, ed., *Extractive and Physical Metallurgy of Plutonium and Its Alloys*, Interscience Publishers, Inc., New York, 1960.
 50. *Reactor Fuel Processing*, 1(3): (July 1958); 1(4): (October 1958); 2(1): (January 1959); and 3(4): (October 1960).
 51. H. M. Feder and N. R. Chellew, U. S. Patent 2,949,390, August 1960.
 52. Oak Ridge National Laboratory, Chemistry Division Annual Progress Report for Period Ending June 20, 1960, USAEC Report ORNL-2983, Sept. 22, 1960.
 53. L. P. Bupp, Chemical Research and Development Operation Monthly Report for September 1960, USAEC Report HW-66960-C, Hanford Atomic Products Operation, Oct. 12, 1960. (Classified)
 54. L. P. Bupp, Chemical Research and Development Operation Monthly Report for October 1960, USAEC Report HW-67254-C, Hanford Atomic Products Operation, Nov. 15, 1960. (Classified)
 55. L. P. Bupp, Chemical Research and Development Operation Monthly Report for November 1960, USAEC Report HW-67532-C, Hanford Atomic Products Operation, Dec. 15, 1960. (Classified)
 56. D. O. Raleigh, Pyrometallurgical Separation of Thorium from Thorium-Aluminum Alloys, USAEC Report NAA-TDR-5689, Atomics International, November 1960.
 57. H. Pearlman, Atomics International, November 1960. (Unpublished)
 58. H. Pearlman, Atomics International, October 1960. (Unpublished)
 59. J. Williams and W. J. K. Wright, British Patent 841,860.
 60. Oak Ridge National Laboratory, Gas-Cooled Reactor Project Quarterly Progress Report for Period Ending March 31, 1960, USAEC Report ORNL-2929, June 21, 1960.
 61. Oak Ridge National Laboratory, Gas-Cooled Reactor Project Quarterly Progress Report for Period Ending June 30, 1960, USAEC Report ORNL-2964, Aug. 22, 1960.
 62. R. H. Barnes and D. N. Sunderman, Apparatus for the Study of Fission-Gas Release from Fuels During Postirradiation Heating at Temperatures

- Up to 1600°C, USAEC Report BMI-1453, Battelle Memorial Institute, July 22, 1960.
63. M. T. Morgan et al., Equipment for the Collection and Pressure Measurement of Fission Gases from EGCR Capsules, in Proceedings of the Eighth Conference on Hot Laboratories and Equipment, San Francisco, California, December 13-15, 1960, USAEC Report TID-7599 (Bk. 2), pp. 458-463.
64. P. Chiotti et al., *J. Metals*, 9: 51-57 (1957).
65. E. S. Makarov and S. I. Vinogradov, *Kristallografiya*, 1: 634-643 (1956).
66. *Reactor Fuel Processing*, 3(4): 32 (October 1960).
67. J. P. DeKany et al., Studies of Corrosion by molten Zinc and Cadmium Systems, USAEC Report ANL-6243, Argonne National Laboratory, October 1960.
68. R. J. Teitel and G. S. Layne, The Dow Aluminum Pyrometallurgical Process—Annual Technical Progress Report for Fiscal Year 1960, Nuclear and Basic Research Laboratory of the Dow Chemical Company, Midland, Michigan.
69. R. E. Johnson and J. D. Chilton, Reprocessing of Thorium-Uranium Fuels by Liquid Metal Extraction, USAEC Report NAA-SR-5506, Atomics International, Dec. 1, 1960.
70. D. O. Raleigh, Preparation of Thorium-Aluminum Alloys by Direct Thoria Reduction, USAEC Report NAA-SR-5689, Atomics International, Dec. 1, 1960.
71. I. L. Jenkins et al., The Use of Molten Calcium in the Processing of Metallic Fast Reactor Fuels, British Report AERE-R-2949, August 1960.
72. *Reactor Fuel Processing*, 2(1): (January 1959).
73. L. Benjamin and R. F. Strickland-Constable, Crystallization on Dilute Metal Solutions, *Acta Met.*, 8: 362-372 (June 1960).
74. T. B. King, Kinetics of Reactions Between Liquid Metals and Liquid Salts, USAEC Report NYO-4808, Jan. 17, 1961.
75. R. H. Wiswall (to USAEC), U. S. Patent 2,936,231, May 10, 1960.
76. Siemens-Planawerke Aktiengesellschaft, British Patent 846,025, Aug. 24, 1960.
77. J. E. Antill (to UKAEA), British Patent 847,912, Sept. 14, 1960.
78. O. N. Carlson et al. (to USAEC), U. S. Patent 2,950,962, Aug. 30, 1960.
79. R. H. Moore (to USAEC), U. S. Patent 2,948,586, Aug. 9, 1960.
80. *Reactor Fuel Processing*, 1(4): 17 (October 1958).
81. G. E. Spangler et al., Apparatus for Zone Refining Highly Reactive Metals, Report AFOSR-TN-60-693, Franklin Institute, July 1960.
82. V. S. Emel'yanov et al., Production and Physical Metallurgy of Pure Metals—Part III, Report JPRS-5145, Aug. 1, 1960.
83. A. J. Darnell et al., Vapor Pressure of Thorium, USAEC Report NAA-SR-4512, Atomics International, Feb. 15, 1960.
84. R. E. Blanco, Chemical Technology Division, Chemical Development Section B, Monthly Progress Report for August 1960, USAEC Report CF-60-9-108, Oak Ridge National Laboratory, Jan. 6, 1961.
85. V. R. Cooper, Quarterly Report, Technology of Nonproduction Reactor Fuels Reprocessing, USAEC Report HW-66968, Hanford Atomic Products Operation, Oct. 3, 1960.
86. V. R. Cooper, Quarterly Report, Technology of Nonproduction Reactor Fuels Reprocessing, USAEC Report HW-65267, Hanford Atomic Products Operation, May 19, 1960.
87. E. S. Occhipinti, Reprocessing of Power Reactor Fuels, Quarterly Progress Report for January 1 to April 1, 1960, USAEC Report DP-491, E. I. du Pont de Nemours & Co., Inc., October 1960.
88. P. M. Kranzlein, Corrosion of Stainless Steel in HNO₃-HF Solutions, USAEC Report DP-486, E. I. du Pont de Nemours & Co., Inc., July 1960.
89. Charles L. Peterson et al., Development of Corrosion-Resistant Alloys for Use as Container Materials for Decladding Solutions or as Welding Alloys, USAEC Report BMI-1459, Battelle Memorial Institute, Aug. 8, 1960.
90. J. J. Bordeaux and G. S. Adams, Corrosion of Alloys in Aqueous Hydrofluoric-Nitric Acid Solutions, USAEC Report IDO-14516, Phillips Petroleum Co., Aug. 10, 1960.
91. N. D. Stolica and G. S. Adams, Corrosion in Neutralized Radioactive Waste, USAEC Report IDO-14531, Phillips Petroleum Co., Sept. 21, 1960.
92. C. D. Scott et al., Fluorox Process: Production of UF₆ in a Fluidized-Bed Reactor, USAEC Report ORNL-2797, Oak Ridge National Laboratory, Oct. 27, 1960.
93. R. E. Blanco, Chemical Technology Division, Chemical Development Section B, Monthly Progress Report for April 1960, USAEC Report CF-60-5-106, Oak Ridge National Laboratory.
94. Oak Ridge National Laboratory, Chemical Technology Division Annual Progress Report for Period Ending August 31, 1960, USAEC Report ORNL-2993, Sept. 26, 1960.
95. E. M. Vander Wall et al., Salt-Phase Chlorination of Reactor Fuels. II. ARCO Process Definition and Scoping Studies, USAEC Report IDO-14525, Phillips Petroleum Co., Oct. 28, 1960.
96. R. W. Dayton and C. R. Tipton, Jr., Progress Relating to Civilian Applications During September 1960, USAEC Report BMI-1469, Battelle Memorial Institute, Oct. 1, 1960.
97. R. W. Dayton and C. R. Tipton, Jr., Progress Relating to Civilian Applications During November 1960, USAEC Report BMI-1480, Battelle Memorial Institute, Dec. 1, 1960.
98. Brookhaven National Laboratory, Nuclear Engineering Division Progress Report for September 1 to December 31, 1959, USAEC Report BNL-595, July 1960.

99. Los Alamos Scientific Laboratory, Quarterly Status Report on LAMPRE Program for Period Ending November 20, 1960, USAEC Report LAMS-2487, December 1960.
100. Oak Ridge National Laboratory, Homogeneous Reactor Program Quarterly Progress Report for Period Ending July 31, 1960, USAEC Report ORNL-3004, November 1960.
101. M. C. Cannon et al., Adsorption of Xenon and Argon on Graphite, USAEC Report ORNL-2955, Oak Ridge National Laboratory, Dec. 12, 1960.

Section

V

WASTE DISPOSAL

Radioactive Waste Handling in the Nuclear Power Industry

The Edison Electric Institute has published a report¹ on radioactive-waste handling from the viewpoint of the nuclear power industry. The report is divided into three sections. Section I contains a brief introduction and the conclusions of the report. Section II presents background information related to the over-all radioactive-waste-handling problem. Section III describes how wastes will be handled at the first six large U. S. nuclear power stations, Shippingport, Rowe, Indian Point, Dresden, Enrico Fermi, and Hallam. The appendixes supply supplementary information in specific areas. Some pertinent conclusions from this report are summarized as follows:

1. The production of radioactive wastes need not impede the development of large-scale and widespread nuclear power generation, provided that waste handling receives intelligent and continuing attention and that radiation protection standards remain substantially at currently recommended levels.

2. Technically feasible methods have been developed or conceived for safely handling all wastes that are likely to be generated by nuclear power reactors and associated fuel processes for at least several decades. Radioactive wastes at nuclear reactor sites can be effectively handled by straightforward processes familiar in the electric power, chemical, or nuclear industries.

3. The intensely radioactive wastes from spent-fuel-recovery plants will contain all but a very small fraction of radioactive material produced in reactors. These wastes will have to be contained for as long as several hundred years, and some very long-lived constituents will require special handling even after this time.

Present containment methods appear to be feasible and economically acceptable for an interim period of 20 years or more. However, eventually, more effective and economical methods will be required. Research and development toward this objective are under way.

4. Although the costs of properly handling radioactive wastes can be a small fraction (1 to 5 per cent) of the total nuclear power costs, the consequences of mishandling them can involve important public health, industrial, and other problems, and, in a broader sense, could deter general acceptance of nuclear power generation.

Operating Experience

Seepage Pits

At ORNL, seepage pits² are used for the disposal of intermediate-level-activity liquid wastes. The use of two waste pits³ (2 and 3) for the disposal of intermediate-level liquid wastes has been limited. Another waste pit (4) has been taken out of service, filled, and covered, and routine long-range monitoring procedures have been initiated. A newly designed covered pit (5) was constructed and placed in operation during June 1960.

From June 1952 through December 1959, 1.53×10^7 gal of waste, containing about 432,000 curies of beta activity, was pumped to the pits (2, 3, and 4). The quantity of specific radionuclides released is summarized in Table V-1. As shown, there was a significant increase in the quantity released during 1959. Of special note is the approximately 20,000 curies of Ru^{103} , 197,000 curies of Ru^{106} , and 25,000 curies of Sr^{90} . The increase was attributed to the experimental processing of short-cooled reactor fuel in the Hot Pilot Plant.

As a result of the increased release to the pits, the amount of Ru^{106} which seeped to the bed of

Table V-1 INVENTORY OF ORNL WASTE-PIT SYSTEM³

Period	Volume, gal $\times 10^3$	Curies								Total rare earths†	Total for the year	Gross beta‡
		Ru ¹⁰³ *	Ru ¹⁰⁶	Cs ¹³⁴ *	Cs ¹³⁷	Zr*	Nb*	Sr ⁸⁹	Sr ⁹⁰			
June 1952	4328		5,000		11,000							11,600
to 1955	2,433		4,400		28,000							25,700
1956	2,779		5,500		18,500			730	1,830	5,400	31,960	33,500
1957	2,902		4,500		10,500			110	420	4,000	19,530	41,800
1958	3,156		2,800		17,000			500	9,800	9,000	39,100	45,400
1959	3,590	19,500	197,400	14,800	65,500	9200	12,600	3300	24,700	52,900	399,900	273,900
Total	15,292	19,500	219,600	14,800	150,500	9200	12,600	4640	36,750	71,300	490,490	431,900

* Accounted for after Aug. 20, 1959.

† Exclusive of Y⁹⁰.

‡ Based on a counting efficiency of 12.6 per cent employed by the ORNL Operations Division.

§ Evaporator concentrate released to pit 2.

White Oak Lake in 1959 was estimated to be 1300 curies. This is to be compared with the estimated 160 curies of Ru¹⁰⁶ released in 1958. The concentration of Ru¹⁰⁶ in several batches of waste pumped to the pits in September 1959 was about 90 $\mu\text{C}/\text{ml}$, or 3.6 times greater than the calculated upper limit of discharge over extended periods of time without exceeding the MPC_w (continuous nonoccupational exposure) to the Clinch River. Subsequent discharge of Ru¹⁰⁶ to the pits was sharply curtailed.

About a third of the ruthenium discharged to the bed of White Oak Lake in 1959 moved into the Clinch River. Although the contribution of ruthenium to the river increased, the amount of strontium entering the river from all ORNL operations decreased, and, consequently, the total discharge consumed only 26 per cent of MPC_w for the Clinch River during 1959.

Land Burial

The ORNL burial ground 4, opened in February 1951, was closed to routine burial operations³ in July 1959. The site encompasses an area of 23 acres. The burial rate during its 8.5 years of operation was slightly over 2.5 acres/year. The exact amount of waste in burial ground 4 is not known. However, the volume buried in 1957 and 1958 was ~25,000 and 337,000 cu ft, respectively. During these years, ORNL produced about 50 per cent of the waste, and other Oak Ridge installations and off-site establishments contributed the remainder. A summary of the solid waste disposed of in burial ground 4 in 1957 and 1958 is given in Table V-2.

Table V-2 SOLID-WASTE BURIALS³ FOR 1957 AND 1958

(Burial Ground 4)

Agency	1957		1958	
	Volume, cu ft	%	Volume, cu ft	%
ORNL	142,300	55.9	158,000	47.0
Y-12	9,500	3.7	14,800	4.4
U. T. Agricultural Experiment Station	4,100	1.6	4,200	1.3
ORINS	1,300	0.5	1,300	0.4
Oak Ridge Process- ing Co.	5,700	2.2	16,100	4.8
Knoxville Iron Co.	4,300	1.7	10,700	3.2
K-25	4,100	1.6		
Off-Site shippers:				
KAPL	25,400	10.0	52,100	15.5
ANL	28,900	11.4	33,600	10.0
GE	6,700	2.6	19,000	5.7
Mound Laboratory	13,800	5.4	10,800	3.2
Radiological Service Co.	3,800	1.5	4,400	1.3
BMI			4,200	1.2
Others	4,800	1.9	7,300	2.2
Total	254,700	100.0	336,500	100.0

Low-Level-Activity Liquid

Waste Handling

The ion-exchange treatment of large volumes of low-level-radioactivity process-water wastes is being studied on a laboratory scale at ORNL.^{4,5} The process consists in adjusting the waste to about pH 12 (making it about 0.01M in NaOH), clarifying it to remove solids, and passing it through a bed of phenolic cation-exchange resin.

A mineral ion-exchange material, clinoptilolite, was tested to compare its breakthrough capacity with phenolic-sulfonic and phenolic-carboxylic type resins for processing this type of waste. It was tested using a feed containing added cesium and strontium and made 0.01M in NaOH ($pH \sim 12$). Gross activity (1 per cent level) broke through at ~ 900 bed volumes of waste treated, compared with 1500 to 2000 volumes for phenolic-sulfonic and phenolic-carboxylic resins. Duolite C-65, a phenolic-phosphoric resin, had a breakthrough capacity of about 1000 bed volumes for removing Cs^{137} , about the same as for the phenolic-only resin.

Coagulant aids were studied to determine their effect on the removal of suspended solids from the effluent of the ORNL low-level-radioactivity liquid waste plant,^{3,6} since approximately 50 per cent of the outgoing activity is associated with suspended solids in the effluent. This plant uses a lime-soda treatment process and handles about 200 to 300 million gallons of process waste water per year, containing 200 to 500 curies of radioactivity. Results of the test with selected coagulant aids were inconclusive. The concentration of the feed solutions and the mode and the point of addition of the coagulants were found to affect coagulation. The coagulant aids did not work well when tested with systems containing complexing agents, such as Versene and polyphosphates.

The application of electrode ionization to the decontamination of low-level-activity aqueous wastes is examined in two reports.^{7,8} A United Kingdom report describes experiments using an influent stream containing sodium salts in the range of $10^{-2}N$ to $10^{-3}N$, with triple- and multi-compartmented cells, the desalting compartments being packed with mixed-bed ion exchangers. In these experiments the amount of salt in the desalted stream was reduced to $1/2000$ of the amount in the influent stream, and in the concentrated effluent it was increased up to 100 times the influent. To give the maximum degree of radioactive decontamination obtainable with electrode ionization, a pretreatment step to remove large amounts of calcium, iron, suspended material, and colloids from the waste solution is considered necessary. In studies at the Japan Atomic Energy Research Institute, an electro-dialyzer unit, used for demineralizing brine water, was used for the treatment of radioactive wastes. From the experiments, it was concluded that the transfer rate of either nonradioactive or radioactive ions through ion-exchange mem-

branes was nearly equal. In a two-stage treatment, the concentration of the effluent from the electro-dialyzer was increased to 100 times the initial feed, and the concentration of the demineralized effluent was decreased to $1/10$ of the initial feed. The current efficiency of this electro-dialyzer unit was over 70 per cent.

The removal of several radioactive species (Mn^{65} , Cu^{64} , As^{76} , and La^{140}) from reactor effluent water by passage through a bed of aluminum turnings⁹ has been demonstrated in the laboratory at Hanford. This phenomenon is believed to be due to the formation of a surface corrosion film on the aluminum turnings upon exposure to the reactor effluent water.

An analysis of the methods employed by ORNL for the disposal of liquid wastes containing beta-gamma emitters has been made.¹⁰ The treatment and methods of monitoring and control are discussed in the report.

Centrifugation¹¹ has been studied at Harwell for the handling of radioactive sludges or flocs from the chemical treatment of medium-level-activity wastes (10^{-4} to $10^{-2} \mu c/ml$). Its potential application to the present methods of sludge treatment at Harwell is explored.

Reduction to Solids

A number of calcination methods for the treatment of high-level-activity liquid wastes are under investigation, including fluidized beds, heated pots, radiant-heated spray towers, and rotary kilns. The use of clays or minerals for the adsorption of cesium and strontium activity and as a matrix material is also being studied. Developments on these methods are reviewed below.

Calcination

At Hanford, fluid-bed calciner studies were continued, operating with simulated acid Purex wastes at feed rates of 12 to 15 liters/hr and using an extended-tip feed nozzle.¹² The significant results of these tests were as follows:

1. Lowering the feed-nozzle position from 1 to 2 in. to 5 in. below the stagnant bed height had the principal effects of increasing the tapped powder bulk density, of requiring about a 10 per cent increase in the fluidizing air flow for operable bed agitation and about a 30 per cent increase in the volume flow ratios of atomizing air to feed so as to prevent lumping at the nozzle,

and of doubling (to about 8 per cent) the amount of fines in the calciner off-gas stream.

2. Calcine was successfully removed from the bottom of the calciner bed rather than from the overflow line. This has the advantage of minimizing buildup of large particles in the calciner because the powder is removed from a location where the larger particles tend to accumulate.

3. Limited success was obtained by locating the feed nozzle at the bottom of the calciner and orienting it vertically upward. This was done to determine the feasibility of using the atomizing gas stream for atomizing the liquid feed and fluidizing the bed.

4. The over-all solids deentrainment factor from the calciner through the roughing cyclone, the condenser, and scrubber is indicated to be >10,000.

The Hanford 8-in. by 10-ft radiant-heat spray calciner¹³ was operated using a caustic-neutralized Purex type waste.¹² The effects of varying feed rate, sugar addition to the feed, and oxygen addition on the characteristics of the calcine from this type of feed material are summarized in Table V-3.

per cent. This is probably the result of a mass action effect wherein the sugar must get its oxygen from the nitrate and sulfate rather than from the surrounding gases. Sugar, or some other form of carbon, is required to calcine caustic-neutralized wastes to a dry nonhygroscopic powder because of the high sodium nitrate content of this waste. The low weight loss in the case of no oxygen addition (compared with a lower feed rate run with oxygen) shows that the residence time is not limiting the degree of calcination as is the chemistry.

In the unagitated batch process¹³ being investigated at Hanford, the waste solution is added to a heated stainless-steel pot at a rate sufficient to maintain some solution, and the contents are subsequently fired to 850 to 950°C. Feeds with relatively high sulfate- and sodium-ion concentrations yield low-melting (800 to 900°C) calcines. The formation of a melt at about 800°C requires a mole ratio of sulfate to salt nitrate of greater than 1 and a sodium molarity greater than about 1.2 times the iron-plus-aluminum molarity. The relative concentrations of iron and aluminum do not affect melt formation.

Table V-3 RADIANT-HEAT SPRAY CALCINER RUNS WITH CAUSTIC-NEUTRALIZED PUREX TYPE WASTE SOLUTIONS¹²

Run conditions			Resulting calcine powder characteristics			
Oxygen rate, liters/min	Sugar conc., g/liter	Feed rate, ml/min	Carbon content, ppm	Weight loss,* %	Amount of sulfate, %	Fraction on walls
10	200	38		4.1	41.0	0.53
10	200	93	1790	5.6	40.8	0.40
10	200	134	2790	6.7	37.1	0.40
10	250	140	2230	6.5	35.5	0.60
14	250	128		5.6	38.2	0.64
0	200	125	2200	2.3	29.3	0.25

* Weight loss upon heating the powder between 300 and 900°C is used as an indication of the degree of calcination achieved.

As shown in Table V-3, the degree of calcination (determined by weight loss) decreases as the feed rate increases. This is the reverse of the feed-rate effect observed with acidic Purex waste. Because the weight loss follows the carbon content, the weight loss upon heating the neutralized waste powder may be attributed in part to the residual carbon content that is burned off.

When no oxygen was introduced in the spray calciner, the weight loss was reduced to 2.3 per cent, and the sulfate content was reduced to 29

The following results are reported^{12,14,15} for studies with simulated Purex type waste performed in the laboratory (3-in.-diameter by 7-in.-high pots) and in the recently completed pilot plant (8½-in.-diameter by 48-in.-high pots):

1. A melt was formed when solid sodium sulfate was mixed with granular fluidized-bed calciner product. The melt's thermal conductivity was 2.5 Btu/(hr)(sq ft)(°F/ft), which was a 20-fold improvement over that of the raw fluid-bed product. The final volume was 158 per cent of that of the fluidized-bed product.

2. A hygroscopic solid was formed when a simulated Purex high-activity-level waste neutralized to 0.8M excess caustic was calcined.

3. A viscous melt was formed at 850°C with a Purex acid waste containing high sulfate and phosphate concentrations.

4. A waste solution simulating one from the interim storage tanks that contain neutralized Purex 1WW waste and solvent washes was pot calcined. At about 850°C the solids partially melted and foamed over. The foaming was attributed either to carbonate decomposition or to the release of gases from the reaction between the melt and the stainless-steel pot internals.

5. Calcining of neutralized wastes acidified with sulfuric acid produced a melt at 900°C with a bulk density of 1.8 g/cm³. In contrast to the run noted under item 4, made with an alkaline waste, there was no foaming of the melt or apparent pot corrosion.

6. Pilot-plant studies corroborated the parameters on melt formation which were established during laboratory studies.

To improve the thermal conductivity of granular calcine, its incorporation in a metal matrix^{14,15} is being examined at Hanford. Aluminum, zinc, cadmium, zinc-tin, and cadmium-tin were found to be unsatisfactory because of their reactions with the sinter product. Where the powder voids of the calcined material were filled with tin, the thermal conductivity of the composite was increased to 8 Btu/(hr)(sq ft)(°F/ft) at 105°F. [Compression of fluidized-bed calcine from Purex type wastes from 1.3 to 1.7 g/cm³ improved the thermal conductivity from 0.08 to 0.2 Btu/(hr)(sq ft)(°F/ft).]

Studies on the use of pot calcination¹³ for the conversion of Purex type wastes to solids are being continued⁵ at ORNL. A synthetic Purex waste containing additional sodium and magnesium ions to decrease sulfate volatility was continuously evaporated and calcined to 900°C in a 4-in.-diameter by 18-in.-long stainless-steel pot calciner. Nitric oxide gas was added, as required, to prevent pressure buildup in the constant-volume system. A volume reduction of almost 10 was achieved. The residue had a bulk density of 1.9 (about 40 per cent porosity). The condensate contained 95 per cent of the total nitrate fed to the system, 47 per cent of the ruthenium, and 0.5 per cent of the sulfate. The consumption of nitric oxide was about 0.4 mole

per liter of waste or 0.06 mole of nitrate in the feed.

In one batch experiment, equal volumes of a synthetic Purex waste and calciner condensate acid were combined and evaporated by a factor of 2 in the presence of nitric oxide. The condensate was decontaminated from ruthenium by a factor of about 10⁴, indicating that this proposed recycle scheme would be satisfactory. In another batch experiment, one volume each of Purex waste and calciner condensate acid was diluted with six volumes of water and evaporated by a factor of 8 in the absence of nitric oxide. The evaporator condensate contained about 1 per cent of the feed ruthenium, indicating that more dilution with water is required to make this proposed recycle scheme satisfactory.

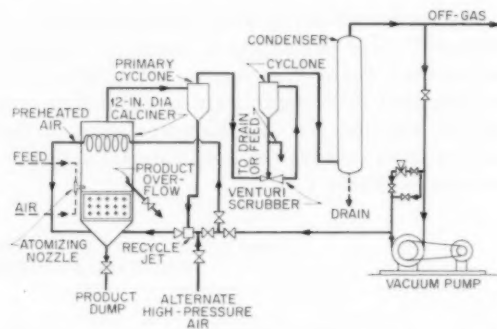


Fig. V-1 Flow sheet diagram of the 12-in. calciner.¹⁷

A new 12-in.-diameter electrically heated fluid-bed calciner unit (see Fig. V-1) is being installed in the ICPP pilot plant to replace the 6-in.-diameter unit.^{16,17} Before the smaller unit was dismantled, the following results were obtained:

1. The distribution of ruthenium between the solids and the off-gases was found to be approximately two parts to the solids and one part to the scrub liquid when the calciner was operated at 400°C and the venturi scrubber liquid was recycled.

2. No special problems appear to exist in the calcination of wastes from the Darex processing of stainless-steel-clad fuel. A bulk density of at least 98 lb/cu ft and a 35-fold volume reduction were achieved.

The ICPP 6-ft-high, 2-ft-square, fluidized-bed calciner has operated satisfactorily (in excess of 500 hr) with the NaK manifold rede-

signed to eliminate the stressed zones that caused failure because of thermal-stress cracking.^{16,17} Depending on operating conditions, the apparent over-all heat-transfer coefficient has ranged from 35 to 150 Btu/(hr)(sq ft)(°F), the higher coefficients being associated with small-bed particle size and high product bulk density.

Excellent fluidization has also been obtained with a calciner-bed air-distributor plate designed with $\frac{3}{8}$ -in.-diameter holes on a 4.5-sq-in. pattern. Each hole is covered by a 2-in.-diameter disk supported on $\frac{3}{8}$ -in.-long tripods to prevent the bed from falling through the plate when fluidizing air is cut off.

The effect of temperature on the volatility of strontium was studied to determine losses in bulk storage. Strontium may be considered essentially nonvolatile since analyses showed <0.001 per cent, the detection limit, volatilized at temperatures up to 1100°C (2012°F).

A 2-in. pulsed-plate liquid-solids contactor¹⁸ is being tested at ICPP for the leaching of fission products from calcined aluminum oxide solids. Extrapolated data^{16,17} on dilute nitric acid leaching of cesium from alumina calcined at 400°C indicate that 99.99 per cent of the cesium can be leached in a continuous contactor. Preliminary data indicate that cesium leaching from alumina calcined at 650°C is more difficult than that from alumina calcined at 400°C. This suggests that a postleaching high-temperature drying step might permit direct ground disposal of calcined wastes.

Two electrostatic precipitators,¹⁶ 1.76 and 4 in. in diameter, were tested at approximately 10- and 25-kv potentials, respectively, for the removal of alumina particulate¹³ from a gas stream. Efficiencies of 99 per cent were found for particles down to 0.6 μ in diameter and approximately 91 per cent for smaller particles when gas loadings ranged in the vicinity of 0.0003 g/cu ft.

Laboratory studies at ICPP have demonstrated the technical feasibility of using mercury cathode electrolysis¹⁹ to effect an appreciable separation of iron, nickel, and chromium from the fission products in wastes resulting from the chemical processing of reactor fuels clad or alloyed with stainless steel. The removal of alloy metal ions from solution by mercury cathode electrolysis permits the alloy constituents and the fission products to be treated as separate wastes. The alloy constituents may be converted to a solid and stored in low-integrity containers with-

out danger of self-heating from fission-product decay. The fission-product waste can be reduced to a very small volume for storage or for recovery of valuable fission products, or it can be converted to a solid for permanent disposal.

Adsorption on Natural Materials

At Hanford the mineral clinoptilolite² continued to be studied in the laboratory and the Micro Pilot Plant for the decontamination of various types of Purex wastes. In the laboratory experiments¹² the 180-cm-long clinoptilolite column was operated at flow rates equivalent to 50 gal/(sq ft)(hr). The column capacity determined from the 50 per cent breakthrough point for cesium was about 600 column volumes of diluted waste, representing 30 column volumes of actual waste. For a synthetic Purex neutralized waste supernatant solution containing a small amount of actual waste and then diluted 1:20 with water, a cesium decontamination factor of $>10^7$ was obtained for 420 column volumes of diluted waste. Breakthrough of Sr⁹⁰ did not occur until well after the Cs¹³⁷ breakthrough. This result is attributed to a reaction between calcite impurity in the mineral and phosphate in the waste. A decontamination factor of at least 10^3 was indicated for rare-earth nuclides, with no breakthrough occurring during the experiment. Alpha emitters were removed to levels below detection.

With a supernatant solution prepared from synthetic Purex 1WW waste, "acid-killed" and neutralized, a cesium capacity of 740 bed volumes of diluted waste (37 bed volumes of undiluted solution) was obtained.¹² This improvement over that obtained above is ascribed to the lower sodium content in the neutralized acid-killed waste. A similar experiment, using influent traced with Sr⁸⁵, gave a column capacity of 620 bed volumes (31 bed volumes of undiluted solution). A decontamination factor of 10^7 was obtained during the first 380 bed volumes (19 bed volumes of undiluted solution).

Trace quantities (0.0012M) of phosphate ion found in aluminum decladding waste are believed to be responsible for the unexpectedly high strontium removal when this type waste is passed through a clinoptilolite column.¹² The reaction of the phosphate with calcite or gypsum impurities in the zeolite could remove strontium from solution independently of ion exchange on the clinoptilolite. To test this, a simulated alumi-

num decontamination waste, traced with Sr^{90} and containing 0.01M phosphate, was passed through a mixed bed of calcite and gypsum. A decontamination factor >200 was attained with this system, which may be compared with a factor of 2 attained in a similar experiment to which no phosphate was added.

In the Micro Pilot Plant experiments,^{12,15} various inorganic ion-exchange materials were tested (see Fig. V-2) for their effectiveness in removing cesium and strontium from condensate

at flow rates of 10 gal/(sq ft)(min) removed Cs^{137} to $<4 \times 10^{-5} \mu\text{c/ml}$, a level below the maximum permissible concentration (MPC) in water. The effluent concentration of Sr^{90} varied from 1 to $3 \times 10^{-6} \mu\text{c/ml}$, which is slightly higher than the MPC_W.

Chelation¹³ is being studied at BNL as a means of keeping interfering ions at a minimum in order to achieve high decontamination factors for cesium and strontium when processing Purex type wastes on mineral clay columns. Experi-

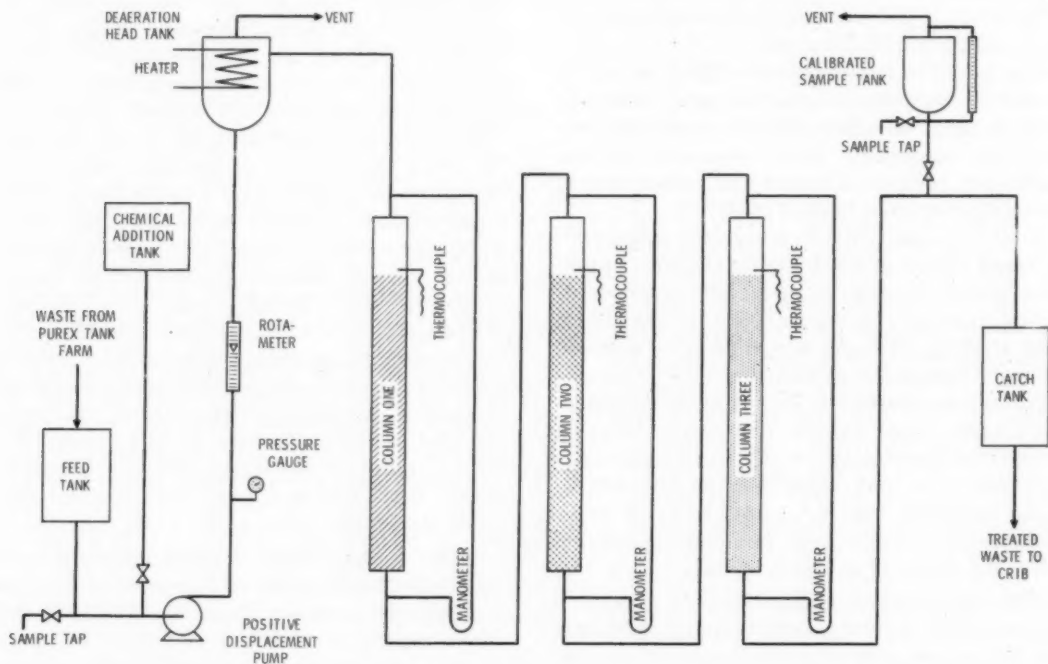


Fig. V-2 Schematic diagram of Hanford Micro Pilot Plant.¹⁴

resulting from the self-boiling of wastes in Purex storage tanks. Runs were made in 1-in.-diameter columns with bed heights varying from 32 to 38 in., generally at ambient temperatures of 25°C. The feed solutions were pretreated for the removal of emulsified and soluble organic impurities (TBP) by passage through activated carbon. The activated carbon does not appreciably remove any of the isotopes studied, but it has improved the efficiency of clinoptilolite for the removal of cesium. Clinoptilolite (treated to remove clay from the crude), Decalso (a synthetic gel type zeolite), and Linde 4A Molecular Sieves (a synthetic crystalline type zeolite), even

ments using citric acid to chelate corrosion products (0.005M iron, 0.0009M chromium, and 0.0008M nickel) from a Purex type waste have shown that decontamination factors for strontium of the order of 10^5 can readily be achieved. It has been shown, however, that further decontamination of the effluent with respect to strontium can be obtained by means of isotopic dilution²⁰ of the very small amounts of strontium in the effluent (which presumably has been chelated since it has passed through the column) and not increase the total strontium to anything more than a very low concentration. An experiment was conducted with a Purex type waste contain-

ing the corrosion products, synthetic fission products ($2.3 \times 10^{-4}M$ strontium) spiked to about 10^7 dis/(min)(ml), and citric acid. Three separate runs were made using 1-ft columns of clinoptilolite, and the concentration of citrate was, respectively, 0.065M, 0.007M, and 0.0825M. The temperature in each test was maintained at 65°C. In each case a decontamination factor of $>10^5$ was obtained. Each of the effluent solutions was then isotopically diluted so that the strontium concentration was raised to the original $2.3 \times 10^{-4}M$ level, and Sr^{90} was added to give 5×10^4 dis/(min)(ml). The solutions were allowed to sit at 40°C for about a week so that the freshly added strontium could equilibrate with the small amounts of chelated strontium. The solutions were then passed through 1-ft columns of clinoptilolite, and decontaminations $>5 \times 10^3$ were achieved in the second ion-exchange step. Total decontamination for each of the three solutions ranged from 1.6 to 5.0×10^3 .

A major problem in an ion-exchange process using influent solutions containing corrosion products is precipitation within the column due to a rise in pH to levels >5.0 . One means of overcoming this difficulty without chelation is to use the hydrogen form of the exchanger, and thus maintain the pH at lower values. Ion exchange under these conditions, however, appears to be relatively ineffective for most of the ions, but strontium is adsorbed to a considerable degree.¹³ A 1-ft column of clinoptilolite passing 4 liters of a Purex type waste containing corrosion products and added Sr^{90} gave a decontamination factor of 2.0×10^6 . The pH of the feed solution was 4.5, and the temperature was maintained at 65°C. In order to investigate the possibility of further decontamination in such a system, the effluent (pH = 3.0) with Sr^{90} increased to 10^4 dis/(min)(ml) was passed through a second 1-ft column. An additional decontamination factor of 3.2×10^3 was obtained for a total decontamination factor of 6.4×10^9 .

Clinoptilolite is also being studied at BNL as a matrix material²⁰ for the preparation of glasses for liquid waste disposal.¹ A number of phosphate glasses have been made with various concentrations of representative waste products. Leaching studies are under way.

Harwell has also reported the composition of glasses²¹ which can be used for incorporating highly active liquid wastes and which appear to be suitable for long-term storage.

Final Disposal Methods

Ground Disposal

Soil chemistry research,¹³ being conducted at Hanford to support the program of ground disposal of low- and intermediate-level-activity liquid wastes, is reviewed in recent reports.²²⁻²⁴ The accumulation and retention of fission products by soil is a result of ion exchange, precipitation, and mineral replacement reactions that occur between the soil constituents and the ions in solution. Good agreement has been found between laboratory and field studies. The order found for the movement of radionuclides through Hanford soil is ruthenium > cesium > strontium > rare earths > plutonium.

Although the seepage pits at ORNL do an effective job in decontaminating the intermediate-level waste stream before it reaches the surface waterways of White Oak Creek and the Clinch River, the use of a soil- or mineral-filled column^{3,25} appears to be very attractive since it would eliminate many of the objections to the present seepage-pit system. The quality of the effluent could be accurately monitored and controlled, and the exact definition of the boundaries of the sorbed nuclides would be established.

The sorptive behavior of various clays, clay minerals, and other minerals for the removal of cesium and strontium was studied. Vermiculites with added phosphate ion were found to be satisfactory for removal of cesium and strontium. Clinoptilolite and Florida pebble phosphate also appear to be promising for column application. The sorptive capacity of minerals was found to vary with mineral structure, ion-exchange capacity, pH of waste solution, saturating cation, heat-treatment of sorbent, and column operating conditions.

Disposal into Salt Formations

The storage of liquid and solid wastes in natural salt deposits continues to be studied experimentally in the laboratory and in the field by ORNL.³ Cooperating in these studies with ORNL are the Geotechnical Corporation, Dallas, Tex., the Department of Sanitary Engineering of the University of Texas, the Applied Physics Laboratory of the U. S. Bureau of Mines, and the Carey Salt Company, Hutchinson, Kans. The field experiments are being carried out in an unused section of the Carey Salt Company mine.

Theoretical heat-transfer studies^{26,27} indicate that the temperature of radioactive wastes stored in salt cavities can be kept within acceptable limits by controlling the age of the wastes and the size of the cavity. Interpolation of theoretical thermal calculations for one- and six-year-cooled wastes indicated that two-year-cooled wastes could be stored in a 10-ft-diameter sphere without boiling. This has been confirmed by the field experiments, one utilizing simulated 7M acid Purex waste and the other utilizing neutralized Purex waste. The heat-production rate being used in these field experiments is equivalent to that of two-year-cooled wastes from fuel irradiated 10,000 Mwd per metric ton of uranium at a specific power of 33 Mw/ton and yielding 800 gal of waste per ton.

Gas production by radiolysis, rather than by chemical interaction with the salt in the storage cavity, is believed to be a more serious problem with the Purex type wastes contemplated.

Disposal by Hydraulic Fracturing into Shale

Tests are under way at ORNL³ to determine the feasibility of injecting large volumes of radioactive wastes into rock formations by hydraulic fracturing. Present well-drilling and test-drilling methods are quite adequate for this proposed disposal operation. Preliminary tests suggest, however, that simple, cheap, clay-cement mixtures can be blended with almost any neutralized-liquid waste, including a heavy load of suspended solids, in such a way that they will set up with sufficient strength in depth to immobilize the waste. Also, it appears that heat dissipation from a thin grout sheet is unlikely to be a problem. Geologically, the sites are not hard to find. Shale or shaly sandstone are among the most common of sedimentary rocks, and, in much of the United States, they are present in flat-lying beds with much simpler and, therefore, more favorable structure than in the test areas in Oak Ridge.

A preliminary experiment was designed to test the testing method and to give some information on the fracture pattern to be expected at relatively shallow depths. A 3.5-in.-OD steel casing was cemented into an existing 300-ft-deep well and slotted at a depth of 290 ft with a sand jet that cut through the casing and out into the shale. Water was then pumped down the well until the shale fractured at a pressure of 3200 psi. The fracture was extended by continuing to pump a well-head pressure of 600 psig.

Once it was clear that the well was taking the injected water easily, Portland cement and diatomaceous earth in equal amounts of volume were added to the water, and a small high-pressure metering pump injected a solution of radioactive cesium into the top of the well casing where it mixed with the grout. A total of 20,000 gal of water, 1370 cu ft of bulk Portland cement, and 1370 cu ft of Litepoz (diatomaceous earth) were pumped into the well. The total volume injected was about 26,000 gal, or 3500 cu ft, to which 25 curies of Cs¹³⁷ and 8 curies of Ce¹⁴⁴ were added.

The grout sheet was found to extend in a nearly horizontal sheet from the test hole. The thickness of the grout sheet is somewhat variable, ranging from 0.03 to 0.005 ft in the cores thus far recovered, but averaging about 0.02 to 0.015 ft.

A second fracturing experiment is planned for ORNL and is to duplicate in scale an actual disposal operation, except that water and a radioactive tracer (Cs¹³⁷) will be used rather than actual waste.

Sea Disposal

The AEC is conducting a project,²⁸ which began Jan. 12, 1961, off the coast of southern California to test the integrity of containers used to confine low-level radioactive wastes during descent to a depth of 1000 fathoms in disposal at sea.¹³

Containers are immersed to 1000 fathoms (6000 ft) and photographed before and during immersion. The tests are conducted in an area of the Santa Cruz Basin, approximately 32 miles southwest of Port Hueneme, Calif. This area was designated by the AEC as a waste-disposal site.²⁸

The Advanced Systems Development Division of Pneumo-Dynamics Corp. of El Segundo, Calif., was awarded a contract by the AEC to conduct the sea tests of containers. Photographic engineering and radiological health services for the tests are provided by Edgerton, Germeshausen & Grier, Inc., of Santa Barbara, Calif., under sub-contract.²⁸

The tests are designed to determine the structural behavior of the various types of containers now used for waste disposal in the sea at depths of 1000 fathoms (pressures up to approximately 3000 psi). Types of containers to be tested at sea include 55-gal drums with the wastes em-

bedded in concrete inside the container, 55-gal drums encased in concrete, and concrete shapes of various sizes. Most of these will be actual containers used by AEC licensees and contractors.²⁸

In a parallel phase of the tests of sea disposal containers, the AEC has contracted with Southwest Research Institute at San Antonio, Tex., to perform laboratory tests of containers.²⁸ Pressure testing and impact testing will be performed on containers of the types now being used and on experimental containers. Tests also will be performed on the various pressure-equalizing devices. The purpose of these laboratory tests is to determine the effects of high pressure on different packaging methods under controlled laboratory conditions. A total of 54 models of containers will be tested by the Institute.

Separation of Specific Isotopes

At ORNL a solvent-extraction process¹³ is under development for recovering megacurie quantities of fission products from reactor fuel-processing wastes. A flow sheet for the recovery of strontium and rare earths has been proposed and is being tested.⁵

The flow sheet, which uses D2EHPA for the solvent, was tested with nonradioactive solutions in miniature mixer-settler equipment. Physical operability was excellent, with no emulsions or precipitates throughout the runs covering the first, second, and third cycles. In the first cycle an iron separation factor of 4.4×10^3 was obtained. In the second cycle, which includes the rare earth-strontium partitioning and the rare-earth stripping steps, 98.2 per cent of the rare earths was recovered as product, with 1.8 per cent of the rare earths being lost to the used organic stream. Separation factors were rare earth/sodium, 9×10^3 , and rare earth/iron, 130. Strontium in the rare-earth product was below the level of analytical detection. In the third cycle, essentially 100 per cent recovery of the strontium may be assumed since strontium losses in the raffinate and used solvent were below the detection limit. From iron analyses, 0.8 per cent of the iron in the third-cycle feed was present in the strontium product; the strontium/iron separation factor was 108.

Hanford is continuing its investigations into methods for recovering Sr^{90} , Tc^{99} , Ce^{144} , and Pm^{147} from Purex wastes.^{13, 18, 29}

For the recovery of Sr^{90} , a lead carrier-oxalate metathesis flow sheet has been developed (solvent-extraction processes are also being studied).³⁰⁻³³ The crude strontium product will be subsequently further purified at the ORNL Multicurie Fission-Product Pilot Plant, the HAPO High-Level Radiochemistry Facility, or the HAPO Hot Semiworks. Two primary separation processes have been found to be practical, and there is little to choose between them. The first scheme uses a high sulfate concentration to precipitate strontium with the cerium-rare earth double sulfates (tartrate complexing being used to prevent ferric sulfate precipitation and to improve decontamination from zirconium-niobium), whereas the other method uses lead sulfate carrier.³² The strontium is next separated from the rare earths by digestion at 90°C with oxalic acid at pH 0.6 to 1.0. The rare earths and lead are precipitated by this treatment while strontium stays in solution. The strontium is then precipitated (as oxalate) by raising the pH of the supernatant to 9 to 10 and digesting at low temperature (<50°C).

To test the flow sheet, two liter-scale hot-cell runs have been made using full-level-scale Purex 1WW waste.³³ The runs were successful in demonstrating the operability of the process with full-level waste and dispelled concern that radiolytic decomposition of reagents would be excessive. Decontamination factors from zirconium-niobium, ruthenium, and cerium were in very good agreement with laboratory tracer-level experiments (no data are given in the report); however, over-all strontium recoveries were lower than expected: the best was 50 per cent. The recovered strontium contained no detectable barium, but the calcium-to-strontium ratio (on a mole basis) was 4 to 1. This concentration of calcium would limit capacity in the Hanford hot-cell ion-exchange purification operation to about 8000 to 9000 curies of Sr^{90} per run.

A series of flow-sheet modifications were explored to reduce the Sr^{90} losses in the oxalate metathesis and product precipitation steps.³³ Of a number of approaches tested, a carbonate metathesis proved to be quite satisfactory. Overall strontium recovery was 85.3 per cent, and decontamination factors from zirconium-niobium, ruthenium-rhodium, cerium, and yttrium were 15, 242, 22, and 58, respectively. A combined 5M sodium hydroxide-1M sodium carbonate metathesis was shown to be somewhat better

than carbonate alone. Strontium losses are still <1 per cent, but the bulk of the lead is also removed. This would be of particular advantage in an integrated flow sheet in which it was desired to recover cerium and/or promethium as well as strontium.

For purification of the crude strontium product, an ion-exchange process has been developed (although it has not yet been tested with full-level feed) which will furnish a strontium better than 99 per cent pure.³³ The crude, containing strontium, calcium, barium, lead, iron, and residual cerium and rare earths, is loaded onto a Dowex 50 X-12 column. The absorbed band is then eluted with pH 8.8, 0.015M EDTA solution at 50 to 60°C. Dosage calculations and the best available resin exposure data indicate that resin degradation should not be a serious problem.

As an interim method for the off-site shipment of the Sr⁹⁰ crude from Hanford to Oak Ridge, adsorption on a bed of inorganic ion-exchange resin contained in a shielded transfer tank appears to be feasible.^{32,33} Decalso YG (an inorganic ion exchanger made by the Permutit Company) and Linde 4A Molecular Sieves were tested. Both adsorbents exhibited surprisingly high capacity for strontium. The Decalso YG loaded, at 50 per cent breakthrough, to about 50 g of strontium per liter of resin. This is equivalent to 4000 curies of Sr⁹⁰ per liter of resin. The capacity of the Linde Molecular Sieves is even higher. The behavior of cerium on Decalso has also been determined since there is about 2 per cent cerium in the crude strontium. Cerium and the other rare earths were found to adsorb just as firmly as strontium. This implies that 2.2-Mev cerium gamma will control the amount of strontium which can be shipped in shielded transfer tanks. Heat transfer will also be a controlling factor.

If the supernatant is pumped from the Purex waste-storage tank for cesium recovery, it is considered relatively easy to recover the technetium (which is also present) by ion exchange. Dowex 1, an anion resin, was found to adsorb over 99 per cent of the technetium.³¹ A micro-pilot-plant-scale ion-exchange run was performed with 100 ml of full-level Purex tank supernatant. The waste was filtered to remove suspended sludge and fed at 1.4 ml/(cm²)(min) to a nitrate-form Dowex 1 X-4 column. After passage of 50 column volumes (all the feed), 98.5 per cent of the technetium had been adsorbed, and the instantaneous loss was still <10

per cent of the feed concentration. The column was then washed with 0.1M nitric acid to remove carbonate and eluted with 8M nitric acid. The bulk of the technetium was readily eluted in about five column volumes with a peak concentration of over 2 g/gal.

Other Literature

A special session of invited papers on radioactive waste management and disposal was held at the 1960 Winter Meeting of the American Nuclear Society³⁴ in San Francisco, Calif., on December 12 to 15, 1960. Summaries of these papers are published in the Society's Transactions. Topics covered include operations at ORNL, the Savannah River Plant, HAP0, and ICPP; the fixation of radioactive wastes in solids; and the disposal of radioactive wastes into deep geologic formations.

The proceedings of the Monaco Conference (see the April 1960 issue of *Reactor Fuel Processing*, Vol. 3, No. 2, page 40) on the disposal of radioactive wastes, held in November 1959, have been published in two volumes,³⁵ containing some 70 papers and covering virtually every aspect of this subject. Several of the papers presented at this Conference have appeared as separate reports.³⁶⁻³⁹

The report of the Sixth AEC Air Cleaning Conference,⁴⁰ held at Idaho Falls, Idaho, in July 1959, is now available. Topics covered include summaries of air-cleaning activities at the various AEC laboratories and contractor operations; waste calcination off-gas studies; ruthenium adsorption on silica gel; problems associated with the testing, handling, storage, and installation of high-efficiency filters; adsorption of fission-product gases; and economic information.

A bibliography⁴¹ on nuclear reactor fuel processing and waste disposal is being prepared by ORNL. Volume 2 (Fission-Product, Poison, and Radioisotope Removal) has been issued. There will be eight main sections, as follows:

- 1.0 Chemistry and Physics of Important Elements
- 2.0 Fission-Product, Poison, and Radioisotope Removal
- 3.0 Fissionable Material — Recovery
- 4.0 Hazards and Protection
- 5.0 Plants and Equipment
- 6.0 Process Chemistry and Engineering

7.0 Surveys

8.0 Waste Disposal

The complete collection includes about 7000 abstracts, nearly all from *Nuclear Science Abstracts*, representing books, bibliographies, symposia, journals, and contractors' topical reports. The material dates from the 1955 Geneva Conference to October 1960.

The text material used as a basis for a series of lectures on radioactive-waste disposal for the International Institute of Nuclear Science and Engineering at ANL has been compiled and issued as a report.⁴² It covers such topics as the origin and management of wastes; the handling of gaseous, solid, and liquid wastes; and ultimate disposal.

Inorganic ion-exchange materials that are very stable to high radiation doses and to elevated temperatures have many possible nuclear energy applications. The preparation on a kilogram scale and a study of the properties of zirconium phosphate, which has cation-exchange properties, are discussed in a United Kingdom report.⁴³ At 300°C, zirconium phosphate was found to have a cation-exchange capacity of approximately 1.6 meq/g.

References

1. Radioactive Waste Handling in the Nuclear Power Industry: A Report of the Technical Appraisal Task Force on Nuclear Power to the Boards of Directors of the Edison Electric Institute, Edison Electric Institute, 750 Third Avenue, New York, N. Y., March 1960; also, *The Forum Memo to Members*, Atomic Industrial Forum, Inc., 7(10): (October 1960).
2. *Reactor Fuel Processing*, 3(3): (July 1960).
3. Oak Ridge National Laboratory, Health Physics Division Annual Progress Report for Period Ending July 31, 1960, USAEC Report ORNL-2994, Oct. 24, 1960.
4. F. L. Culler et al., Chemical Technology Division Annual Progress Report for Period Ending August 31, 1960, USAEC Report ORNL-2993, Oak Ridge National Laboratory, Sept. 26, 1960.
5. F. L. Culler, Chemical Technology Division Report for October 1960, USAEC Report CF-60-10-118, Oak Ridge National Laboratory, Oct. 31, 1960.
6. T. Subbaratnam et al., Studies of the Use of Coagulant Aids in the Lime-Soda Treatment of Large-Volume Low-Level Radioactive Liquid Waste, USAEC Report CF-60-7-17, Oak Ridge National Laboratory, Aug. 22, 1960.
7. D. C. Sammon and R. E. Watts, An Experimental Study of Electrodeionization and Its Application to the Treatment of Radioactive Wastes, British Report AERE-R-3137, June 1960.
8. M. Ito and M. Nishidoi, Treatment of Radioactive Wastes with Ion-Exchange Membrane Electrolyzer (Abstract in English), Japanese Report JAERI-1012, Japan Atomic Energy Research Institute, April 1960.
9. W. B. Silker, The Effect of Temperature and Flow Velocity on the Decontamination of Reactor Effluent Water with Aluminum, USAEC Report HW-62874, Hanford Atomic Products Operation, Dec. 1, 1959.
10. Y. Feige et al., Analysis of Waste-Disposal Practice and Control at ORNL, USAEC Report CF-60-8-72, Oak Ridge National Laboratory, Oct. 4, 1960.
11. J. de Bruyn and K. W. Pearce, Radioactive Sludge Handling, British Report AERE-M-713, August 1960.
12. D. W. Pearce, ed., Research and Development Activities, Fixation of Radioactive Residues, Quarterly Progress Report for July-September 1960, USAEC Report HW-67334, Hanford Atomic Products Operation, Oct. 15, 1960.
13. *Reactor Fuel Processing*, 4(1): (January 1961).
14. D. W. Pearce, ed., Research and Development Activities, Fixation of Radioactive Residues, Quarterly Progress Report for January-March 1960, USAEC Report HW-65209, Hanford Atomic Products Operation, Apr. 15, 1960.
15. D. W. Pearce, ed., Research and Development Activities, Fixation of Radioactive Residues, Quarterly Progress Report for April-June 1960, USAEC Report HW-66571, Hanford Atomic Products Operation, July 15, 1960.
16. J. I. Stevens, ed., Idaho Chemical Processing Plant, Radioactive Waste Disposal Projects, Technical Progress Report for October-December 1959, USAEC Report IDO-14526, Phillips Petroleum Co., Aug. 31, 1960.
17. J. I. Stevens, ed., Idaho Chemical Processing Plant, Radioactive Waste Disposal Projects, Technical Progress Report for January-March 1960, USAEC Report IDO-14530, Phillips Petroleum Co., Sept. 9, 1960.
18. *Reactor Fuel Processing*, 3(4): (October 1960).
19. M. E. McLain and D. W. Rhodes, Stainless-Steel Process Wastes. I. Removal of Alloy Metals from Waste Solutions by Mercury Cathode Electrolysis, USAEC Report IDO-14533, Phillips Petroleum Co., Sept. 30, 1960.
20. L. P. Hatch et al., Brookhaven National Laboratory, Aug. 1, 1960. (Unpublished)
21. J. R. Grover and B. E. Chidley, Glasses Suitable for the Long-Term Storage of Fission Products, British Report AERE-R-3178, July 1960.
22. W. H. Bierschenk, Techniques for Estimating the Specific Retention Properties of Hanford Soils, USAEC Report HW-61644, Hanford Atomic Products Operation, Aug. 20, 1959.

23. L. L. Ames, Jr., Anion Replacement Reactions for the Removal of Strontium from Aqueous Solutions, USAEC Report HW-66383, Hanford Atomic Products Operation, July 5, 1960.
24. D. W. Bensen, Review of Soil Chemistry Research at Hanford, USAEC Report HW-67201, Hanford Atomic Products Operation, Aug. 10, 1960.
25. T. Tamura and E. G. Struxness, Removal of Strontium from Wastes, USAEC Report CF-60-10-43, Oak Ridge National Laboratory, Nov. 28, 1960.
26. Oak Ridge National Laboratory, Health Physics Division Annual Progress Report for Period Ending July 31, 1959, USAEC Report ORNL-2806, Oct. 29, 1959.
27. J. Crowell and F. L. Parker, A Thermal Problem Associated with Underground Storage of Radioactive Wastes, USAEC Report ORNL-3002, Oak Ridge National Laboratory, Nov. 17, 1960.
28. AEC To Test Containers Used in Sea Disposal of Radioactive Waste, AEC Press Release D-4, Jan. 5, 1961.
29. L. P. Bupp, Chemical Research and Development Operation Monthly Report for May 1960, USAEC Report HW-65459-C, Hanford Atomic Products Operation, June 15, 1960. (Classified)
30. L. P. Bupp, Chemical Research and Development Operation Monthly Report for June 1960, USAEC Report HW-65854-C, Hanford Atomic Products Operation, July 15, 1960. (Classified)
31. W. H. Reas, Chemical Research and Development Operation Monthly Report for July 1960, USAEC Report HW-66237-C, Hanford Atomic Products Operation, Aug. 19, 1960. (Classified)
32. W. H. Reas, Chemical Research and Development Operation Monthly Report for August 1960, USAEC Report HW-66644-C, Hanford Atomic Products Operation, Sept. 16, 1960. (Classified)
33. L. P. Bupp, Chemical Research and Development Operation Monthly Report for September 1960, USAEC Report HW-66960-C, Hanford Atomic Products Operation, Oct. 12, 1960. (Classified)
34. *Trans. Am. Nuclear Soc.*, 3(2): (December 1960).
35. *Proceedings of the Scientific Conference on the Disposal of Radioactive Wastes, Monaco, November 16-21, 1959*, Vols. I and II. (Available from the National Agency for International Publications, Inc., 801 Third Avenue, New York, 1960.)
36. R. H. Burns, Radioactive Waste Control at the United Kingdom Atomic Energy Research Establishment, Harwell, British Report AERE-M-649, March 1960.
37. C. W. Mawson et al., Waste Management and Monitoring at Chalk River, Canadian Report CRL-59 (AECL-987), November 1959.
38. J. I. Stevens, Treatment, Processing, and Future Disposal of Radioactive Wastes at the Idaho Chemical Processing Plant, USAEC Report IDO-14502, Phillips Petroleum Co., Mar. 7, 1960.
39. L. C. Watson et al., The Permanent Disposal of Highly Radioactive Wastes by Incorporation into Glass, Canadian Report AECL-1072, September 1960.
40. Sixth AEC Air Cleaning Conference, Idaho Falls, Idaho, July 7-9, 1959, USAEC Report TID-7593, October 1960.
41. T. F. Connolly, Fission Product, Poison, and Radioisotope Removal, Bibliography on Nuclear Reactor Fuel Reprocessing and Waste Disposal, USAEC Report ORNL-2971 (Vol. 2), Oak Ridge National Laboratory, Oct. 18, 1960.
42. W. A. Rodger, Radioactive Waste Disposal, USAEC Report ANL-6233, Argonne National Laboratory, September 1960.
43. B. E. Chidley and J. R. Grover, Preparation and High-Temperature Properties of Zirconium Phosphate Ion-Exchange Materials, British Report AERE-R-3357, September 1960.

Section VI

PRODUCTION OF URANIUM, THORIUM, PLUTONIUM, AND THEIR COMPOUNDS

Uranium

Uranium Trioxide Production

The continuous pot denitration process for converting uranyl nitrate to uranium trioxide has been tested and evaluated in plant-scale operation at NLCO. The process involves the continuous introduction of uranyl nitrate into an agitated pot and simultaneous withdrawal of the oxide product.¹ The existing installation has been operated on a sustained basis at production rates averaging 550 lb of uranium trioxide per hour per unit, which is a significant improvement over batch processing. However, variation in heat-transfer rates has resulted in variable production rates. Heat transfer occasionally decreases to the extent that the production rate² declines to a level of 400 lb/hr.

Operation of the continuous pot has occasionally been complicated by the unexpected presence of crystals in the feed system. Investigation has shown that the presence of ammonium nitrate in concentrated uranyl nitrate greatly influences the temperature at which crystals form.³ The crystallization temperature is considerably elevated by the presence of ammonia in concentrations exceeding 15,000 ppm. Ammonium uranyl nitrate has properties distinctly different from those of uranyl nitrate. The fact that it decomposes without going through a dough stage, producing a chemically active orange oxide, makes it an interesting possibility as a feed to the denitration process.

Uranium Tetrafluoride Production

Fluid-Bed Operation. The production of uranium tetrafluoride from uranium dioxide is currently being carried out in screw-agitated reactors. Since fluid-bed reactors offer improved gas-solid contact and temperature con-

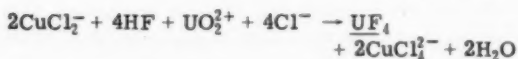
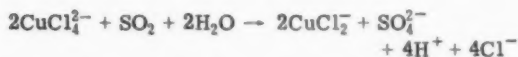
trol, considerable attention has been directed toward employing fluid-bed reactors in the preparation of uranium tetrafluoride. Green salt has been produced using very small excesses (5 to 10 per cent) of hydrogen fluoride in a five-stage reactor.⁴ A pilot-scale fluid-bed hydrofluorinator employing an internal tapered mandrel has been briefly tested.⁵ The tapered mandrel is used to provide a constant superficial gas velocity throughout the reactor. Provided that the gas velocity does not greatly exceed that required for incipient fluidization, a close approach to piston flow of the solids may be achieved. The effect of this flow behavior is that adequate fluidization may be achieved without gross mixing of the fluidized particles. Therefore high production rates may be achieved in a single tapered reactor; whereas several stages may be required in a reactor of conventional design. A description of the principles of fluidization in a tapered column has been published with specific reference toward employing this technique in the fluid-bed conversion of uranium trioxide to uranium tetrafluoride.⁶

Steady-state operation of a single-stage fluid-bed hydrofluorinator employing an internal tapered mandrel has produced uranium tetrafluoride with an average assay of 90 per cent.⁵ It has been impossible, however, to improve the operation so as to produce green salt of acceptable purity with the single-stage unit. Owing to recurrent plugging in the top of the reactor, it was necessary to employ high fluidization-gas velocities which precluded any approach to piston flow in the bottom of the reactor. In a preliminary run in the existing single-stage reactor, designed to simulate two-stage operation, average product analyses as good as 96.7 per cent UF_4 , 0.7 per cent AOI (ammonium oxalate insoluble content), and 2.6 per cent UO_2F_2 were achieved. The two-stage fluid-bed hydrofluori-

nator incorporates a well-mixed first stage, and a second stage utilizes the tapered internal mandrel. Additional studies will be made on this two-stage concept.

Recovery of Uranium Tetrafluoride from Scrap Materials. Uranium-bearing scrap material is now being processed at the Metals Recovery Plant, Fernald, Ohio, to produce metal-grade uranium tetrafluoride by the Winlo process.⁷ The plant was converted to utilize this process in treating both low-grade (magnesium fluoride scrap) and high-grade (calcined uranyl ammonium phosphate or black oxide) wastes.⁸

Magnesium fluoride scrap is treated with a sulfuric acid solution, using manganese dioxide as an oxidant. The uranium is extracted from this solution into a 5 vol.% solution of amine in kerosene containing 2.5 vol.% primary decyl alcohol. The loaded organic is stripped with 3N hydrochloric acid in one stage at an organic-to-aqueous ratio of 20 to 1. Copper sulfate and hydrofluoric acid are added to the strip solution. The uranium is precipitated as $\text{UF}_4 \cdot \frac{3}{4}\text{H}_2\text{O}$ by heating the solution to 90°C and bubbling sulfur dioxide gas into the solution. The reactions involved in the precipitation step can be represented by the following equations:



The reduction of hexavalent uranium to tetravalent uranium is accomplished by the catalytic action of the cuprous chloride ion, which is continuously regenerated from the cupric chloride ion by the addition of sulfur dioxide during the precipitation step. The uranium tetrafluoride product is a high-density (3 g/cm³) material that is easily filtered. Copper is recovered from the filtrate by plating onto scrap iron.

Calcined uranyl ammonium phosphate and uranosic oxide (U_3O_8) can be converted to uranium tetrafluoride by dissolution in hydrochloric acid using nitric acid as an oxidant, followed by the Winlo process for precipitating hydrated uranium tetrafluoride.

Dehydration to approximately 0.1 per cent water is readily accomplished by heating to

440°C in a closed vessel. Hydrated green salt can be reduced by magnesium to give metal of acceptable quality if it is blended with production green salt prior to reduction. The preheat times were longer for the blended green salt than for production green salt. Dehydrated uranium tetrafluoride alone can be reduced to give acceptable metal if it is ground to 20- μ -size particles.

Fluidized-Bed Coating of Uranium Dioxide

The encapsulation of individual uranium dioxide particles with either metal or ceramic coatings by fluidized-bed techniques has been demonstrated by workers at BMI. A description of the procedures used in coating uranium dioxide particles with various metals was described in an earlier Review.⁹ This technique has been extended to coating of particles with a layer of aluminum oxide.¹⁰ Process conditions were established in a Vycor reactor 30 mm in diameter with uranium dioxide particles ranging from 44 to 350 μ .

Aluminum oxide was successfully deposited on uranium dioxide by reacting a mixture of water vapor and aluminum chloride at a bed temperature of 1000°C. Essentially stoichiometric quantities of aluminum chloride and water vapor were fed to the reactor. Hydrogen was used as the main fluidizing gas, primarily to avoid oxidation of the uranium dioxide during the initial phase of the coating operation. The rate of aluminum oxide deposition on a 100-g bed of uranium dioxide was about 3 g/hr. By increasing the concentration of reactants in the fluidizing gas and increasing the bed temperature to 1400°C, coating rates as high as 12 g/hr have been achieved. The fraction of alumina formed as coating on the particles ranged from 50 to 75 per cent; the remainder appeared as entrained dust.

Uniform, dense alumina coatings about 5 to 150 μ thick were successfully obtained. The coated particles were resistant to nitric acid leaching, to oxidation in air at 1000°C, and to thermal cycling from 300 to 1370°C. Although the process conditions have not been optimized, it appears from a consideration of the preliminary work that a commercially feasible process of this type can be realized.

Uranium Hexafluoride Production

A complete compilation of data on the physical properties of uranium hexafluoride has been

published with references to 150 sources.¹¹ Items covered include (1) data on the thermodynamic properties and transport phenomena of uranium hexafluoride and (2) binary- and ternary-phase equilibrium systems.

The production of uranium hexafluoride from uranium tetrafluoride by oxidation with dry air or oxygen in a continuous fluidized-bed reactor is under investigation at ORNL.¹² The oxidation proceeds according to the reaction $2\text{UF}_4 + \text{O}_2 \rightarrow \text{UF}_6 + \text{UO}_2\text{F}_2$. The uranyl fluoride by-product is recycled to the feed stream after reduction to uranium dioxide and hydrofluorination to uranium tetrafluoride. A description of the Fluorox process development work has appeared in an earlier Review.⁸

One of the main reasons for investigating this process was the high cost of fluorine incurred in other methods for producing uranium hexafluoride. Fluorine costs become particularly significant when fluorine is used in small quantities. A cost study of the Fluorox process has been made to obtain an estimate of the manufacturing cost for converting feed-materials-grade uranium tetrafluoride to cascade-grade uranium hexafluoride.¹² The estimate was made on a fully integrated facility, including uranyl fluoride recycle, and a purification step to remove accumulated metal fluoride impurities from the process stream. The total manufacturing cost was reported to be \$0.29 per pound of uranium processed for a plant with a throughput equivalent to 5000 tons of U_3O_8 per year. The chemical cost was calculated to be \$0.06 per pound of uranium processed. The chemical cost for converting uranium tetrafluoride to uranium hexafluoride with fluorine has been estimated to be \$0.09 per pound of uranium. The authors conclude that where there are existing facilities for uranium hexafluoride production by the use of fluorine, there does not appear to be justification for considering the Fluorox process as an alternative. The Fluorox process should receive consideration if a new facility is planned with a throughput <5000 tons of U_3O_8 per year.

Production of Uranium Metal

from UF_6 -Source Uranium Tetrafluoride

Ground magnesium fluoride has been the standard liner material in uranium metal production when the reduction charge contained uranium tetrafluoride produced by the hydrofluorination of uranium dioxide. However, UF_6 -

source uranium tetrafluoride must be reduced in electrolytically fused dolomite, a relatively expensive liner material, because reductions in ground magnesium fluoride produce low yield and poor quality derbies. It was found that when moisture was added to either the magnesium fluoride liner or the green salt, successful reductions were achieved.² Blending the UF_6 -source green salt with hydrated uranium tetrafluoride (Winlo process) proved to be an effective method of adding moisture to the reduction charge. Average derby yields of 96 per cent were obtained with a blend containing 20 per cent Winlo green salt. Excellent derby yields were obtained when 1.0 per cent moisture was added to the slag liner. In no case was the hydrogen level in the metal increased by the addition of moisture either to the uranium tetrafluoride or to the slag liner.

Thorium

Although no large-scale thorium production plants have been placed into operation, considerable knowledge and technology are available if the need arises. Reference 13 summarizes some of the various processes that are capable of supplying high-purity thorium metal on a tonnage basis. Included in this survey are descriptions of four processes: (1) calcium reduction of thorium oxide, (2) metallic reduction of thorium tetrachloride or thorium tetrafluoride in the presence of zinc, (3) electrolytic reduction of the tetrachloride in a fused-salt bath, and (4) sodium amalgam reduction of thorium tetrachloride. Each process flow sheet is evaluated on the basis of costs and product specifications.

The electrolysis of thorium tetrafluoride in a sodium chloride-potassium chloride eutectic is a principal method of thorium production in the U.S.S.R. A comprehensive study¹⁴ of the electrolysis mechanism and the physicochemical properties of the electrolyte was undertaken to optimize the quality and yield of the thorium product. The electrolyte composition varied during the electrolysis because of chlorine evolution at the anode resulting in an accumulation of fluorides as NaF or KF in the electrolyte. Owing to the production of these fluoride salts, some of the thorium fluoride became combined in complex compounds of the type $(\text{Na}, \text{K})_x \text{Th}_y \text{F}_{x+4y}$.

On prolonged electrolysis the maximum yield of thorium metal was obtained only when the thorium concentration in the electrolyte exceeded 40 to 45 wt.%. At lower concentrations the yield dropped sharply, and alkali metals were liberated at the cathode. When the volume concentration of current was increased from 10 to 70 amp per kilogram of electrolyte (0.5 to 4 amp/cm² cathode current density), the metal yield was increased from 15 to 75 per cent, and the current efficiency was increased from 9 to 56 per cent. The quality of the metal product was also improved by operating with a current density >1.5 amp/cm²; the amount of fine powder formed at the cathode decreased from 75 to 25 per cent of the total metal deposit. The optimum operating temperature was 680 to 700°C.

Since the amount of electrolyte entrained in the cathode deposit amounted to 75 per cent of the metal weight, considerable thorium within the electrolyte was lost when the metal crystals were cleaned by a water wash. Therefore a means of compacting the cathode deposit to decrease the quantity of electrolyte removed with the metal was developed.¹⁵ The result was a decrease in the quantity of entrained electrolyte to 25 per cent of the metal weight and an increase in the over-all metal yield. The automatic compacting device involved pressing an auxiliary cathode onto the main rotating cathode. The dendritic crystals are firmly compacted and squeezed without dropping from the cathode.

Under optimum conditions, coarsely crystalline thorium metal was obtained with a metal yield of 75 per cent and a current yield of 56 per cent. Approximately 90 per cent of the coarse crystalline metal was -65 + 325 mesh. The metal was >99.5 per cent pure, with the major impurities being oxygen and fluoride. The rare-earth content in the metal was significantly reduced from the original concentration in the starting thorium fluoride.

Plutonium

Preparation of Plutonium Chloride and Reduction to Metal

The main objection to the use of plutonium fluoride in plutonium metal preparation is the high neutron density resulting from intense alpha radiation of the fluorine atoms. By using a halogen of higher atomic number, the neutron exposure would be reduced more than by any

reasonable shielding. Therefore a process was developed at HAPO¹⁶ which involved the continuous chlorination of plutonium dioxide by phosgene, followed by the bomb reduction of plutonium trichloride to metal with calcium.

Plutonium oxalate hexahydrate was prepared by reacting a 1M solution of plutonium nitrate with a solution containing 1M oxalic acid and 0.25M hydrogen peroxide. The peroxide served to convert the plutonium to the tetravalent state. The oxalate precipitation was conducted in a 4-in.-diameter vessel equipped with an air-driven stirrer to prevent settling of the precipitate. The optimum conditions of the oxalate preparation required a 0.1M excess of oxalic acid in the supernatant stream. The free nitric acid concentration in the plutonium nitrate stream was 3.5M to 5M. If these conditions were not maintained, the precipitate would not filter readily, and the plutonium losses would exceed the values of 2 to 5 per cent usually experienced.

The wet oxalate was converted to plutonium dioxide by calcining at 250 to 350°C in a screw reactor. The oxide preparation was stopped short of conversion to stoichiometric plutonium dioxide in order to ensure the production of a free-flowing powder that would be readily chlorinated.

Several chlorinating agents (hydrogen and hydrogen chloride, carbon tetrachloride, and chlorine-carbon monoxide mixture) were evaluated, and all were found to be less reactive than phosgene. The use of phosgene permitted a choice of a 100°C lower temperature for an equivalent reaction rate or a higher chlorination rate at the same temperature as the other reactants.

The chlorination was conducted in a vibrating-tube reactor with a 4° slope. Plutonium dioxide was fed to the upper end of the reactor at a rate of 250 g/hr. Phosgene gas, preheated to 200°C, entered at both ends of the tube at a rate of 6 moles per mole of plutonium dioxide. As the oxide powder vibrated down the tube, it was heated during a 40-in. path to temperatures rising to 500°C. The average residence time in the chlorinator was 35 min. The conversion to plutonium trichloride was consistently 98 per cent.

The plutonium trichloride was reduced to metal in a magnesia crucible by reaction with calcium. Iodine was used as a booster. Firing was initiated by heating in an induction coil until the bomb skin temperature reached 700°C.

The metal was prepared in batches ranging from 30 to 1400 g, with yields averaging 98 per cent. Impurities in the metal usually totaled <0.2 per cent.

It was found that the presence of moisture in the plutonium trichloride up to 0.5 per cent would not affect the reduction operation. Good mixing of the reduction charge was not necessary if the plutonium trichloride were on top.

A comparison of the neutron radiation from plutonium fluoride and plutonium trichloride showed that the neutron radiation from the fluoride was 64 times that of plutonium trichloride.

Recent Review Publications

Reference 17 contains a two-volume treatise on the chemistry, purification, and metallurgy of plutonium. The books present the details of the research concerned with the preparation of high-purity plutonium during the years 1940 to 1944. Of historical interest is the fact that initial work was done with tracer quantities of material and that chemical plants were designed and constructed on the basis of results of experiments with only micrograms of plutonium.

A collection of papers on the extractive and physical metallurgy of plutonium, presented at the 1959 Annual Meeting of the American Institute of Mining, Metallurgical, and Petroleum Engineers, has been published.¹⁸ Most of the papers are review articles on the following selected topics: methods for the preparation of plutonium metal^{18a}; calcium reduction^{18b}; solvent-extraction separation of plutonium^{18c}; and preparation of plutonium halides^{18d}. A comprehensive annotated bibliography on all aspects of plutonium technology by Wilkinson^{18e} has been included. In addition, there are eight papers on the physical metallurgy of plutonium metal and alloys.

Grenoble Plutonium Metallurgy Conference

In April 1960 the Plutonium Metallurgy Conference was held in Grenoble, France. The proceedings of the conference, which are scheduled to be published soon, should provide an excellent source of information on plutonium. Most of the papers presented at this international conference were devoted to the physical metallurgy of plutonium metal and alloys and have been reviewed elsewhere.¹⁹ A paper de-

scribing the historical development of the calcium reduction process for the preparation of plutonium metal from a halide was presented.²⁰ The processes described were developed at Los Alamos Scientific Laboratory during the years 1943 to 1946. The methods and equipment used to prepare metal of greater than 99 wt.% purity on a 1- to 500-g scale from either plutonium trichloride or plutonium tetrafluoride were described in considerable detail.

Plutonium metal of high purity has been prepared at ANL by fused-salt electrolysis using plutonium anodes containing 1000 to 4000 ppm impurities.²¹ The electrolyte was 7 mole % plutonium tetrafluoride in a LiCl-KCl eutectic mixture. The electrolyses were carried out in Hastelloy C and Vycor cells at 400 to 470°C with molybdenum and tantalum cathodes. Impure plutonium metal was cast under vacuum into anodes $\frac{1}{4}$ in. in diameter and 4 in. long. The applied potential ranged from 0.16 volt to 2 volts, and initial current density ranged from 0.6 to 8.3 amp per square centimeter of anode area. Purified plutonium (65 ppm impurities) collected at the cathode in solid crystalline deposits. Metal buttons were collected by melting the cathode deposits in molten LiCl-KCl or NaCl-KCl eutectic at 700°C. Over-all recoveries of 60 per cent were achieved in the electrolysis runs.

There was no significant difference between the metal deposited in the delta or delta-prime phases. Plutonium that was deposited under conditions of low current density was slightly more contaminated than metal deposited with high current density. The use of the NaCl-KCl eutectic as a meltdown salt for the preparation of metal buttons is beneficial since the salt seems to reduce contamination of certain metal impurities, which is not done in the LiCl-KCl system.

High-purity plutonium prepared by bomb reduction contains at least 300 ppm impurities, whereas the electrolytic metal contained only 65 ppm analyzed impurities. The major remaining impurities were hydrogen, carbon, oxygen, and uranium. The purity of the metal prepared by collecting the metal as a solid cathode deposit was definitely superior to the metal obtained by an electrefining process utilizing a molten cathode described in the previous issue of *Reactor Fuel Processing*.⁹

References

1. *Reactor Fuel Processing*, 3(4): 48-49 (October 1960).
2. J. W. Simmons, ed., Summary Technical Report for the Period April 1, 1960, to June 30, 1960, USAEC Report NLCO-810, National Lead Co. of Ohio, Aug. 11, 1960. (Classified)
3. National Lead Co. of Ohio, Summary Technical Report for the Period July 1, 1960, to September 30, 1960, USAEC Report NLCO-820, Oct. 28, 1960.
4. *Reactor Fuel Processing*, 1(2): (April 1958).
5. S. N. Robinson and S. Simecek, Pilot Plant Fluid-Bed Hydrofluorination, in Process Development Quarterly Progress Report for July-September 1960, USAEC Report MCW-1459, pp. 43-47, Mallinckrodt Chemical Works, Nov. 1, 1960.
6. R. P. Levey, Jr., et al., Fluid-Bed Conversion of UO_3 to UF_4 , *Chem. Eng. Prog.*, 56: 43-48 (March 1960).
7. E. O. Rutenkroger et al., Production of UF_4 from Refinery Scrap Materials, *J. Metals*, 12: 866-870 (November 1960).
8. *Reactor Fuel Processing*, 3(1): (January 1960).
9. *Reactor Fuel Processing*, 4(1): (January 1961).
10. M. F. Browning et al., Alumina Coating of UO_2 Shot by Hydrolysis of Aluminum Chloride Vapor, USAEC Report BMI-1471, Battelle Memorial Institute, Oct. 25, 1960.
11. R. DeWitt, Uranium Hexafluoride: A Survey of the Physico-Chemical Properties, USAEC Report GAT-280, Goodyear Atomic Corp., Aug. 12, 1960.
12. C. D. Scott et al., Fluorox Process: Production of UF_6 in a Fluidized-Bed Reactor, USAEC Report ORNL-2797, Oak Ridge National Laboratory, Oct. 27, 1960.
13. R. G. Orrison, Union Carbide Nuclear Co., Y-12 Plant, Dec. 18, 1959. (Unpublished)
14. A. I. Yevstyukhin et al., Investigation of the Electrolytic Production of Thorium, in Production and Physical Metallurgy of Pure Metals, Part 1, Report JPRS-2920, pp. 1-34, July 5, 1960.
15. A. I. Yevstyukhin and G. A. Leont'yev, Design of an Electrolyzer with Automatic Compacting Cathodes for Electrolysis of Fused Thorium Salts, in Production and Physical Metallurgy of Pure Metals, Part 1, Report JPRS-2920, pp. 35-43, July 5, 1960.
16. M. J. Rasmussen and H. H. Hopkins, Jr., Preparation of Plutonium Metal Via the Chloride State, paper presented at the American Chemical Society Meeting, New York, September 11-16, 1960.
17. C. A. Thomas, ed., The Chemistry, Purification, and Metallurgy of Plutonium, USAEC Report MUC-JCW-223 (Bks. 1 and 2), December 1944.
18. Metallurgical Society of AIME, *Extractive and Physical Metallurgy of Plutonium and Its Alloys*, edited by W. D. Wilkinson, Interscience Publishers, Inc., New York, 1960:
 - 18a. I. L. Jenkins et al., Alternative Routes for the Conversion of Plutonium Salts to Metal and Their Recovery Problems, pp. 25-40.
 - 18b. R. D. Baker and W. J. Maraman, Calcium Reduction of Plutonium Halides to Metal, pp. 43-58.
 - 18c. E. L. Christensen et al., Distribution of Plutonium and Selected Impurity Elements Between Nitrate Solutions and Tri-*n*-butyl Phosphate, pp. 75-88.
 - 18d. J. G. Reavis et al., The Preparation of Plutonium Halides for Fused-Salt Studies, pp. 89-100.
 - 18e. W. D. Wilkinson, Annotated Bibliography, pp. 263-307.
19. *Reactor Core Materials*, 3(3): 7-16 (August 1960).
20. W. J. Maraman and R. D. Baker, Calcium Reduction of Plutonium Halides to Metal, International Conference on the Metallurgy of Plutonium, Grenoble, France, April 19-22, 1960, Paper No. 38.
21. B. Blumenthal and M. B. Brodsky, The Preparation of High Purity Plutonium, International Conference on the Metallurgy of Plutonium, Grenoble, France, April 19-22, 1960, Paper No. 3.

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